Chapter 2

Subject Overview and Research Methodology

Integration of passive components is an effective technique to cater the unrelenting need for faster, smaller and better electronic circuits. Several technologies are being developed for integration of passives, which are briefly discussed in the preceding Chapter. The low temperature co-fired ceramic (LTCC) is one amongst the preferred technologies for passive integration owing to the favourable dielectric properties. The major advantage of this technology is that it can integrate a good number of passive components even if it means integration of dissimilar materials. However, this technology is limited by the materials incompatibility of the host glass-ceramics with the high Q-ceramics, yield issues, lack of design tools and lack of standardization. The technology is also limited by the narrow range for capacitors and inductors, low Q of the inductors and low tolerance issues for all, resistors, inductors and capacitors. These sets of problems have received much attention in the recent years. As a result, the consortiums like Advanced Embedded Passive Technology (AEPT), National Electronics Manufacturing Initiative (NEMI), and National Aeronautics and Space Administration (NASA) - NASA Electronic Parts and Packaging (NEPP-NASA) have also paid attention to the passive integration issues in LTCC as well as the Printed Wire Board (PWB) technologies. However, it is seen that their present focus is on the integration of resistors and capacitors in LTCC.
Various stand-alone materials systems are presently under investigation for their use in LTCC. Some of these systems are even available commercially. On the other hand, it is believed from the available literature that the issue on integration of inductors in LTCC has not been taken-up by these consortiums, specifically the NEPP-NASA\textsuperscript{1-3}. However, the research groups worldwide (including NEMI) have published good amount of archived value publications on this subject. Integration of inductors is mired with difficulties. Today, the integration of inductors in LTCC is accomplished within the host dielectric material and built using the multilayer signal lines and a ground plane. Such inductors have limited Q, low self-resonant frequency (SRF), low inductance and high losses. These issues can be circumvented by the use of ferrite materials in LTCC, which is lagging mainly due to development of special materials and processes. The quality of inductors in LTCC would improve if ferrites could be integrated.

The first part of this Chapter justifies the use of ferrites and explains the importance ferrite integration in LTCC. Thus, the Chapter explicitly surveys the approach other than use of ferrite material and addresses the gaps. Further, the Chapter continues with the survey of previously published work, also describing attempts to integrate ferrites in LTCC. This survey brings out the need for different types of ferrite materials to address the requirements of wide range of passive components required at high frequencies. Prior to this, a brief overview on LTCC technology from the viewpoints of LTCC processing is presented. Finally, the discussion pertaining to the different routes for preparation of ferrites and their characterization are discussed in Section 2 and 3 of this Chapter, respectively.

2.1 Overview of LTCC Technology

LTCC is a multilayer fabrication process that uses glass-ceramic tapes and conducting pastes for preparing the circuits. The use of glass-ceramic material causes reduction in co-firing temperature below 900°C, presenting major advantage of using Ag, Au and their alloys for interconnections; in fact also allows use of all other functional materials used in thick film hybrid technology. This, on one hand reduces the process cost, and on the other expands the technical capability by allowing use of materials for buried passive components. The process also allows attachment of post-fire passive components. This integration of passive components bestows significant advantage in terms of package size, reliability, cost and manufacturability on LTCC and is one of its key features.
The other important feature of LTCC is its high frequency (HF) capability even up to 100 GHz due to low dielectric constant and low loss materials. Surely, LTCC confirms with almost all the requirements of the packaging needs discussed above. Figure 2.1 presents a schematic representation of typical LTCC package.

![Fig. 2.1: Schematic representation of LTCC package allowing integrated passive components](image)

The advantages of LTCC other than integration of buried passive components are listed below:

- Reliability due to ceramic processing
- Low dielectric loss and better control over dielectric properties
- HF capabilities in microwave and millimeter wave frequency range
- Capability of packaging of Si chip together with other technology devices
- Multilayer or 3D circuit design capability
- Can handle fluidic, optical, mechanical and electrical signals simultaneously
- Microsystems devices can be fabricated in LTCC
- Close thermal expansion coefficient to Si, GaAs etc.
- Compatibility with flip chip, wire bonding, Surface Mount Technology (SMT) processes
- Package preparation flexibility including hermetic sealing

There are, however, some perceived disadvantages of LTCC:

- High shrinkage after co-firing and its tolerance cause process difficulties
- Limited range for passive components due to materials limitations
- Higher cost than polymeric packages
- Low thermal conductivity of tapes as compared to ceramic materials
- Non-flexible packages

There are, however, ways to overcome some of the disadvantages. For example, the heat can be routed through thermal via to the outer world, and there are special processing methods which can make the shrinkage as low as zero in X-Y direction. More discussion about some of the process and applications related issues are discussed below.

2.1.1 LTCC Fabrication Process

The LTCC green tapes are prepared by uniformly casting the inorganic powder into polymeric materials using tape-casting technique. The slurry of the casting material is composed of glass-ceramic mixture or composites in binders and organic solvent. This as-prepared slurry is cast to obtain glass/ceramic ‘green’ (unfired) tape and is put together with Mylar support. The package preparation process starts with cutting of green tape to required size and pre-baking at a specified temperature. The package fabrication is usually initiated by preparing via holes, cavities and alignment holes on each single layer individually. These holes are mostly prepared by either mechanical punching, or laser burning process and the diameter varies between ~50µm and 500µm. The intended electrical via are then filled with silver or gold paste, either by stencil printing method or by pressurizing the paste into the via holes. The stencil printing is done using metal/polymer squeeze while vacuum is applied below the sample. Usual thick film screen printing is then employed to print metallization layer and buried passives. The minimum line width of the printed conductors is about 100µm. Each single layer then passes through an optical inspection. Next, all such individually processed layers are aligned with help of registration pins, and stacked after removing supporting Mylar. This method gives registration accuracy within ~10µm. Automatic video alignment is also employed sometimes, which gives slightly improved alignment accuracy. After removing the registration area, whose utility is now over, the stacks are laminated using uniaxial heated press or isostatic laminator. The latter is always preferred due to its ability to retain cavity as via shapes. The individual circuits are then singulated and co-fired at 850 to 900°C peak temperature following a recommended firing cycle. Sometimes, singulation is done after co-firing using diamond wheel cutting machine. The main
characteristic of sintered LTCC package is its all round shrinkage. Free or unconstrained sintering offers approximately 12 - 16 ± 0.3% and 15 - 25 ± 0.5 % shrinkage in $X/Y$ and $Z$-direction respectively depending on the composites used for preparation of LTCC green tape. The integrated LTCC substrate is then available for post-fire processing, which may include print-fire sequences for brazing, attachment of external components, BGA preparation etc. After the completion of all such processing, the substrate is ready for chip attachment and sealing. Figure 2.2 presents the common process sequence for the preparation of LTCC structures.

Fig. 2.2: LTCC fabrication process
2.1.2 Applications of LTCC

By far, the most explored application of LTCC has been for HF circuits. The main reason behind this is the low loss, compact 3D circuits at reasonable cost offered by this technology. Many reports are available that discuss LTCC HF components and circuits from 1GHz to 40GHz, and some even up to 100GHz frequency. LTCC modules are most used as front-end modules for mobile phones, Wireless Local Area Networks (WLAN), Local Multi Point Distribution Systems (LMDS), Various RF modules, Radars, Antennas etc. The major advantage that LTCC offers over conventional implementation of high frequency circuits is its capability to integrate passives in 3D, satisfactory isolation methods, small size antenna and their integration capability, compatibility with MMIC packaging etc. Another important area of LTCC applications is that of sensor packaging; especially the MEMS devices. Although Si chips can integrate most of the circuits required for MEMS devices, in practice obtaining such integrated smart devices for all applications is prohibitively costly due low volumes. This difficulty can be overcome with the help of modularity. LTCC technology is most compatible with such modular sensor electronics. Further, LTCC is capable of handling optical, fluidic and electrical signals. LTCC technology has also been used in Microsystems applications. Indeed, micro valve actuators, flow sensors, pressure sensors and eddy current proximity sensors have been fabricated using LTCC structures.

With a very wide range of applications, LTCC shows promise for true integration of microelectronic circuits including passives, HF circuits as well as various Microsystems in the near future. With respect to the lack of materials limitation for passive integration in LTCC, the work reported in this thesis is a step towards in overcoming the current limitations. The need for integration of magnetic components in LTCC remains an important field of research which has not been taken-up seriously until now. Two main, and technologically important applications are of interest are sought in this Thesis. The integration of inductors in LTCC is one among them, which also caters to the other applications, such as, filters that contain an inductive component. Therefore, the next Section of this Chapter discusses the reported inductors in dielectric LTCC. The second important applications pertain to the integration of non-reciprocal devices, such as circulators or isolators, which are amongst the bulky components in today’s HF electronics. The Section following inductor discusses non-reciprocal devices.
2.2 Integrated Inductors in LTCC Dielectrics

Integrated inductors in LTCC are primarily realized using the efficient use of multi-layer and multi-winding inductance in the host LTCC dielectrics. The dielectric material serves as a carrier material and does not contribute to the inductance value directly. These inductors primarily rely upon the concept of mutual inductance between multi-layer conductor (signal) lines and ground plane. These inductors are susceptible to influences caused by ground plane and signal lines. These effects have to be considered while designing the inductor. The integrated inductors in LTCC are built using screen printing or direct write techniques and can be combined with resistors/ capacitors to form RLC network. Integrated inductors in LTCC are typically formed using one of two design topologies. One, the planar design is a meander, circular or square spiral inductor with 50 to 150 \( \mu \text{m} \) line widths. The second is a 3D-helical design \( i.e. \) a stacked structure with one turn on each layer. The integrated inductors fabricated using spiral or 3D-helical topologies usually result in 1 to 200 nH inductance values, which is appropriate for their use in RF/ microwave applications. A description on these inductors is given in the following Subsections.

2.2.1 Planar Inductors

Planar inductors are divided into meander and spiral structures. Examples of both the topologies in an LTCC substrate are shown in Figure 2.3.

![Design topologies of planar integrated inductors in LTCC](image)

**Fig.2.3:** Design topologies of planar integrated inductors in LTCC \(^{10} \) (a) Meander, (b) circular spiral, (c) Square / rectangular spiral

Meander inductors are easiest to fabricate and offer least inductance values as compared to their counterparts. The inductance value of these inductors is directly proportional to the meander length. These inductors are limited in inductance values due to adverse
magnetic-field orientation of adjacent line segments. These inductors are usually used in low inductance and delay line applications.

The circular/ square-spiral inductors are also easier to design, simulate and fabricate as the meander inductors. The inductance values of these inductors are limited to few nano-Henries, which depends on line width, line spacing and number of turns. The inductance of rectangular spiral inductors is about 20% higher compared to the circular inductor of same dimensions, whereas the quality factor is higher for circular inductors. Any low-profile spiral inductor with micro-Henry inductance values are difficult to fabricate due to materials properties associated with the carrier material. Each additional turn of the spiral inductor causes a non-linear resistance growth due to increasing winding diameter. In addition, the spiral inductors have disadvantage of poor performance due to RF resistance which resulted longer traces of the conductor. In general, RF resistance reflects the skin and proximity effects. At frequencies starting from 1 MHz, the current flowing through the inductor concentrates on the surface of the conductor material (called skin depth $\delta$), which significantly increases the inductor resistance. For any signal carrying conductor, the skin depth is given by the equation:

$$\delta = \frac{1}{\sqrt{\pi \mu f k}}$$

(2.1)

where,

- $\mu$ is effective permeability of the material
- $k$ is the electrical conductivity (Siemens/meter)
- $f$ is the frequency (in Hertz)

Therefore, the sheet resistance, $R_s$ ($\Omega/\square$) of the conductor associated with the skin depth for a given frequency is given by:

$$R_s = \frac{1}{\delta k}$$

(2.2)

The resistance of a rectangular line for a given frequency is thus defined as:

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† Inductors with inductance in the micro-Henry are usually required in power electronics applications. Although power electronic applications are not the topic of prime discussion in this thesis, this limitation of planar inductors is mentioned for completeness.
\[ R(f) = \frac{kIR_s(f)}{2(w+t)} \]  \hspace{1cm} (2.3)

where, 
\( l, w \) and \( t \) are conductor’s length, thickness and width, respectively, in meters.

Thus, Equation 2.3 signifies that wider the lines, the lower is the resistance for a given frequency. Therefore, the spiral inductors occupy larger area, and must be designed with additional area to protect it from parasitic effects. The conductor losses described above can be reduced to some extent by using higher electrical conductivity materials, such as, copper.\(^\ddagger\) The inductance values are also affected in the following way due to conductor effects. The spiral coils over wider area extends the resulting magnetic field far past the device's physical boundaries. This severely affects the inductance value due to the distortion of inherent magnetic field which is present in the vicinity of the device\(^9\). This also increases the possibility of cross-talks between the devices. In addition, the inductance is also reduced due to the ground plane under the spiral coils. The ground plane, as well as the connection of the coil centre to the outer pad causes several coupling capacitances which also affect the behaviour of the inductor. This can be understood from the equivalent circuit model of 2.5 turn spiral inductor integrated in LTCC, as shown in Figure 2.4\(^11\). Each turn of the spiral coil gives concentrated inductance \( L_{1\ldots n} \), conductive losses \( R_{i\ldots n} \), coupling capacitance \( C_{1\ldots n} \) and transmission line segment, which associates different parasitic effects as described above.

![Fig. 2.4: Equivalent circuit model of 2.5 turn spiral inductor integrated in LTCC\(^11\)](image)

For the spiral inductor, a remedy to suppress ground plane effects is to place ground plane away from the inner diameter of the spiral coil. On the other hand, influence of the coupling capacitance can be reduced by using low-\( k \) dielectric material. These as-

\( \ddagger \)Copper is not preferable in LTCC due to oxidation issues.
pects of spiral inductors significantly affect the performance and miniaturization criteria causing preference to the helical inductors over the spiral inductors, mainly due to higher quality performance\textsuperscript{12}.

\subsection*{2.2.2 3-D inductors}

Helical coils can be arranged horizontally or vertically on the layer stack in LTCC. The 3D-helical topology requires lesser and shorter conductor traces than planar spiral inductors. Examples of different topologies of 3D helical inductors in an LTCC substrate are shown in Figure 2.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.5}
\caption{3D-helical integrated inductors in LTCC\textsuperscript{10} (a) horizontal solenoid, (b) vertical square solenoid, (c) sandwich square, (d) vertical circular solenoid, (e) sandwich circular-design topology}
\end{figure}

To obtain higher performance in 3D helical inductors, it is important to keep metal structures, particularly power and ground planes, well away from the core inductor layers, again due to associated parasitic effects. This can be understood from the equivalent circuit model of the 3D-helical inductor integrated in LTCC for both shunt and series connections, as shown in Figure 2.6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.6}
\caption{Equivalent model of 3D-helical inductor integrated in LTCC\textsuperscript{11}}
\end{figure}
In Figure 2.6, the inductance \( L \) represents the lumped part of the total inductance of the coil and \( R \) contains the frequency dependent conductor losses. \( C_1 \) and \( C_2 \) describe the capacitive coupling between the multilayer windings. It is believed from the simulation that the capacitors \( C_1 \) and \( C_2 \) are only sensitive to line width, coil diameter and turn to turn distance and are independent of the number of windings. \( C_2 \) is responsible for the first self resonance. Thus, the Self Resonant frequency (SRF) of an inductor is very much depends on the line widths and materials permittivity, which must be kept as small as possible. The higher parasitic capacitance lowers the measured SRF, as clear from the Equation 2.4.

\[
SRF = \frac{1}{2\pi\sqrt{LC}}
\]  

(2.4)

Thus, reducing the inductance or capacitance raises the SRF. The parasitic capacitance also contributes to the Q-factor\(^{13}\). On the other hand, the inductance reduces due to the ground plane, as in the case of planar spiral inductor. In general, both designs of integrated inductors in LTCC results in limited performance either at the expense of SRF, Q-factor, inductance or larger foot-prints of the device. Table 2.1 provides a detailed comparison of the reported planar spiral and 3D helical inductors integrated in LTCC.

<table>
<thead>
<tr>
<th>Inductor type (^{ref.})</th>
<th># of turns</th>
<th>Height (( \mu )m)</th>
<th>Size (mm(^2))</th>
<th>( Q_{\text{max}} )</th>
<th>SRF (GHz)</th>
<th>L(_{\text{eff}}) (nH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D Spiral(^{14})</td>
<td>2</td>
<td>182.88</td>
<td>---</td>
<td>37 @ 1.3GHz</td>
<td>2.90</td>
<td>4.8 @ 1.30 GHz</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>365.76</td>
<td>---</td>
<td>47 @ 1.3GHz</td>
<td>3.20</td>
<td>6.1 @ 1.30 GHz</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>548.64</td>
<td>---</td>
<td>57 @ 1.3 GHz</td>
<td>3.25</td>
<td>6.7 @ 1.30 GHz</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>182.88</td>
<td>---</td>
<td>28 @ 0.8 GHz</td>
<td>1.50</td>
<td>11.4 @ 0.80 GHz</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>365.76</td>
<td>---</td>
<td>34 @ 0.8 GHz</td>
<td>1.60</td>
<td>14.7 @ 0.80 GHz</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>548.64</td>
<td>---</td>
<td>41 @ 0.8 GHz</td>
<td>1.65</td>
<td>16.6 @ 0.80 GHz</td>
</tr>
<tr>
<td>2D Spiral(^{15})</td>
<td>2</td>
<td>---</td>
<td>8.35</td>
<td>81 @ 1.86 GHz</td>
<td>4.48</td>
<td>5 @ 1.86 GHz</td>
</tr>
<tr>
<td>2D Square Spiral(^{16})</td>
<td>4.5</td>
<td>200.00</td>
<td>6.25</td>
<td>---</td>
<td>1.10</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>400.00</td>
<td>6.25</td>
<td>---</td>
<td>0.96</td>
<td>44.6</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>200.00</td>
<td>6.25</td>
<td>---</td>
<td>0.75</td>
<td>43.6</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>200.00</td>
<td>6.25</td>
<td>---</td>
<td>0.85</td>
<td>42.2</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>400.00</td>
<td>6.25</td>
<td>---</td>
<td>0.83</td>
<td>56.6</td>
</tr>
</tbody>
</table>
### Table 2.1

<table>
<thead>
<tr>
<th>Type</th>
<th>$h(2l):$</th>
<th>$h(6l):$</th>
<th>Specific Resistivity of Conductor Paste</th>
<th>Conductive Cross-section</th>
<th>Skin Effect</th>
<th>Proximity Effect</th>
<th>Eddy Current in Ground Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D Spiral</td>
<td>182.80</td>
<td>548.64</td>
<td>4.09 @ 1.9 GHz</td>
<td>31.53 @ 1.9 GHz</td>
<td>5.1</td>
<td>9.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.49</td>
<td>38.0 @ 1.9 GHz</td>
<td>5.1</td>
<td>9.17</td>
<td></td>
</tr>
<tr>
<td>3D Helix</td>
<td>182.88</td>
<td>548.64</td>
<td>36 @ 1.0 GHz</td>
<td>48 @ 1.0 GHz</td>
<td>7.6 @ 1.0 GHz</td>
<td>8.9 @ 1.0 GHz</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.64</td>
<td>31.15 @ 1.0 GHz</td>
<td>5.1</td>
<td>9.17</td>
<td></td>
</tr>
<tr>
<td>3D Helix</td>
<td>182.8</td>
<td>548.64</td>
<td>89 @ 1.32 GHz</td>
<td>93 @ 1.15 GHz</td>
<td>8.7 @ 1.32 GHz</td>
<td>9.6 @ 1.15 GHz</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.81</td>
<td>18.49 @ 1.15 GHz</td>
<td>5.1</td>
<td>9.17</td>
<td></td>
</tr>
</tbody>
</table>
| Both types of integrated inductors are available for use in LTCC, as evident from Table 2.1. The parameters, such as, specific resistivity of the conductor paste, conductor cross-section, skin effect, proximity effect, eddy current in a ground plane etc. have direct influence on inductor properties with increased operating frequency, as described earlier in this Chapter. As a result, the integrated inductors in LTCC have very low inductance values (typically less than 10 nH) at frequencies greater than 50-100 MHz. While, high
value inductance range 100 to 200 nH is typically obtained at frequencies below 50 MHz. Therefore, these inductors are specifically used in applications in which very low inductance values are required, such as, for example, microwave delay lines. Further, the integrated inductors in LTCC usually have tolerance around ± 10 %. All these aspects of the integrated inductors in LTCC stand in the way for higher performance and miniaturized RF/microwave applications. Furthermore, the micro-Henry inductors are difficult to realize in the LTCC due to large profile or thickness. Clearly, an innovative approach is needed to increase the inductance and quality factor of the integrated inductors in LTCC. The following points summarize the major reasons for adopting a different approach:

- **Limited RF/microwave applications** because of very low inductance (< 10 nH), although GHz range SRF can be obtained
- **Limited RF/microwave applications** because of very low SRF (< 50 MHz), although appropriate inductance (100-200 nH) values can be obtained for RF/microwave applications
- **Larger dimensions of the components** and low inductance density
- Parasitic components dominate with increasing frequency
- **Constraints in designing** - one or more resonance appear without ground plane and larger distance between inductor and ground plane

The development of new materials, and, simultaneously, new designs are required to circumvent the above mentioned problems. Each of these approaches faces significant technological challenges to remain competitive in terms of performance and miniaturization criteria established for LTCC. These approaches are discussed in Section 2.4 onwards of this Chapter.

### 2.3 Existing Integrated Non-reciprocal Devices in LTCC Dielectrics

Microwave non-reciprocal devices, such as, circulators are essential components for telecommunication applications because it offers simultaneously low insertion loss to transmit microwave energy from one of its port to an adjacent port while isolating the signal from all other ports to protect microwave modules. These components are still relatively bulky for the present day, modern electronics. Further, these devices are conventionally produced at high temperatures (> 1400 ºC) following standard processing of
microwave garnet materials, which proves costly. The advancements in LTCC process and technologies, allows fabrication of miniaturized microwave modules along with the integration of circulators, isolators\textsuperscript{22-23}. Despite this fact, however, there are only one or two reports in literature that demonstrate integrated circulators or isolators utilizing LTCC dielectric material. The primary reason behind this is, ferrites and garnets continue to be the first choice materials for these applications, owing to their non-reciprocal behaviour. The designers, therefore, continue to use discrete devices. The preference for these devices stems from the gyromagnetic behavior of the ferrite materials which is beyond the reach of dielectric materials. The gyro-magnetic behaviour of the elementary magnetic dipole or the uncompensated electron spins of the ferrite material allows the non-reciprocal behavior of the ferrite when they become magnetized. Despite the fact that dielectric materials do not provide such advantage, an integrated $K_u$ band transmitter module has been shown in LTCC that consist of two T/R switches, one phase shifter, one attenuator, one power amplifier and a circulator\textsuperscript{22}. Another example is realization of front-end module in LTCC for wireless local area network (WLAN) antenna with high isolation characteristics\textsuperscript{23}. The circulator referred here is a 15-17 GHz microstrip line circulator of size of $7.5 \times 6$ mm. It occupies more area than monolithic microwave integrated circuit (MMIC). These results indicates major drawback in the size of the device. This issue signifies the limitation of using dielectric material for integrated non-reciprocal applications in LTCC along with probably a poor performance of these devices at microwave frequencies with their ferrite counterparts.

2.4 Ferrites: Materials Approach and their Magnetic Properties

Materials for magnetic components, such as, RF inductors and microwave circulators are of prime interest for this thesis. The technological challenges for integrated inductors in LTCC dielectrics are low range of inductance, which can be increased to some extent at the expense of SRF and \textit{vice versa}. Higher inductance is possible with materials having permeability larger than one. Magnetic materials, such as, ferromagnetic metals and ferrites are seen as a potential option. However, it is ferrites that are preferred for both applications in RF/microwave frequencies. The properties which have made ferrites so useful at these frequencies are: permeability and resistivity. The high resistivity of ferrites enables an electromagnetic wave to penetrate the material and the magnetic field component of the wave thus interacts with the magnetic moment of the
ferrite. This offers ferrites an extra degree of freedom to obtain the desired microwave properties beyond the reach of other competent magnetic materials, such as, ferromagnetic metals. Further, the electromagnetic interaction of ferrites is revealed by strong induction due to high permeability of the material at microwave frequencies. Thus, these materials have found wide-spread use as cores for inductors and transformers at RF/microwave frequencies. Finally, when ferrites are magnetized, they become non-reciprocal and are used to build circulators and isolators, for telecommunication systems, such as, radar, mobile telephone relay stations etc.

Ferrites are categorized as cubic-tetragonal, spinel, hexaferrites and garnets, which play an important role in signal processing applications in the frequency ranges starting from kilohertz to hundreds of gigahertz. For each particular application many material properties play an important role. For example, microstructure of these materials governs the quantities, such as, permeability, coercive force and losses. All these properties stems from the structural properties, position as well as the valence state of the magnetic ions in the particular compound. The importance of microstructure in terms of grain growth and porosity is discussed in the Section 2.8.2 while in the next Subsection we discuss the magnetism and magnetic properties in spinel and hexaferrites, which are of particular interest in this Thesis. The magnetism in spinel and hexaferrite stems from the super exchange interaction between the magnetic ions. These properties of the ferrites are analyzed through the use of the Néel model of either two or three magnetic sublattices. The model is applied to describe the properties of both spinel and hexaferrites.

### 2.4.1 Magnetism and Magnetic Properties of Spinel Ferrites

A large number of ferrites have spinel crystal structure. Single or the combination of the divalent metal ions forms the spinel crystal structure of ferrites with general formula $MO.Fe_2O_3$, where $M$ represent one or more divalent metal ions such as Mg, Mn, Fe, Co, Ni, Cu, Zn etc. It is formed by a closed packed $fcc$ array of larger $O^{2-}$ ions with interstices partly filled by metal cations. The tetrahedral ($A$ site) and octahedral ($B$ site) types of holes are formed by the oxygen anions (cf. Fig. 3.2). Further, due to the larger electronegativity of the oxygen, ionic type of bonds prevails in all spinel ferrites. Spinel ferrites are classified as normal, inverse or random spinels, based on the configuration of divalent metal ions and trivalent iron ions. 

\[24\]
• *Normal spinels*, in which divalent metal ions occupy *A sites* and ferric ions (Fe$^{3+}$) are on the *B sites*, a net electrostatic charge zero, thus minimizing electrostatic energy.

• *Inverse spinels*, in which divalent metal ions occupy *B sites* together with half the Fe$^{3+}$ ions, the other half being on the *A sites*

• *Random spinel*, in which both divalent metal ions and Fe$^{3+}$ ions occur on the *A* and *B sites*

*Néel Model for Spinel Ferrite*$^{25}$:

Ferrimagnetism in ferrites can be understood from the relative magnitude and sign of the interaction between magnetic dipoles, *i.e.* the *A-A*, *B-B* and *A-B* interaction. These interactions are defined in terms of the molecular field coefficients $\lambda_{aa}$, $\lambda_{bb}$ and $\lambda_{ab}$, which is negative in case of ferrites. However, the *A-B* interaction is usually much stronger than either of the other two. Therefore, the spins associated with *A sites* are aligned anti-parallel to those in the *B sites*. Then all spins within *A sublattices* (and also *B sublattices*) are aligned parallel to one another despite the weak negative interaction that favors anti-parallel alignment within each sublattices. This is significant in that the magnetic moments of the trivalent Fe ions in sublattice *A* cancel those of the trivalent Fe ions in the sublattices *B* in an inverse spinel. The net magnetic moment of the spinel ferrite then equals the magnetic moment of the divalent ions in the *B sites*.

The ferrimagnetic property explained by the Néel model can be evident by the measurement of the magnetizations of the various spinel ferrites. A magnetic moment that is considerably less than the total magnetic moment of the constituent ions is observed. This discrepancy can be accounted for only by the configuration of oppositely magnetized *A* and *B sublattices* as proposed by Néel. Hence, Fe$^{3+}$ ions distributed over these two sites cancels each other giving rise to reduction in the observed magnetic moment. The net magnetic moment arises only from the divalent metal ions, which gives rise to the magnetization in the ferrites. Table 2.2 presents the saturation magnetic moment for several spinel ferrites.
Table 2.2: The saturation moment of several ferrites in Bohr magnetons

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Total moment</th>
<th>Ferrimagnetic moment (calc)</th>
<th>Observed moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$Fe$^{3+}$O$_4$</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Fe$^{3+}$Fe$^{3+}$O$_4$</td>
<td>14</td>
<td>4</td>
<td>4.2</td>
</tr>
<tr>
<td>Co$^{2+}$Fe$^{3+}$O$_4$</td>
<td>13</td>
<td>3</td>
<td>3.3</td>
</tr>
<tr>
<td>Ni$^{2+}$Fe$^{3+}$O$_4$</td>
<td>12</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu$^{2+}$Fe$^{3+}$O$_4$</td>
<td>11</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>Mg$^{2+}$Fe$^{3+}$O$_4$</td>
<td>10</td>
<td>0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The more details on the crystal structure and their symmetry sites are discussed in the experimental section of spinel ferrite (NiCoZn ferrite), i.e. Chapter 3.4.2.1.

2.4.2 Magnetism and Magnetic Properties of Hexaferrites

Hexagonal magnetic oxides are also a class of ferrimagnetic materials. Hexaferrites crystal structures were first derived from the magnetoplumbite crystals (PbFe$_{12}$O$_{19}$). Hexaferrites are composed of divalent alkaline earth metal ions, $Me$ (Ba or Sr) and Fe$^{3+}$ ions. The Me$^{2+}$ ions are large, as is the O$^{2-}$ ions, and the barium ion always replaces oxygen in the lattice. On the other hand, Fe$^{3+}$ occupies the interstices between the oxygen positions. The unit cell of the hexaferrites contains tetrahedral, octahedral as well as the trigonal bipyramidal sites. More details on the crystal structure and their symmetry sites are discussed in the experimental section of hexaferrites ($M$ and $Z$-hexaferrites) in the Chapter 3 and 4, respectively. The constituent ions of the magnetoplumbite can also be changed to yield a special ferrimagnetic property. The chemical composition diagram is shown in Figure 2.7, and the chemical relationship between the hexaferrites is given in Table 2.3.
Table 2.3: Chemical relationship of hexaferrites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Interrelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$2\text{Me}^{2+} \cdot 2\text{Fe}_2\text{O}_4$ or $2\text{MeO} \cdot 2\text{Fe}_2\text{O}_3$</td>
<td>S</td>
</tr>
<tr>
<td>M</td>
<td>$\text{Ba}^{2+}2\text{Fe}<em>{12}\text{O}</em>{19}$ or $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$</td>
<td>M</td>
</tr>
<tr>
<td>W</td>
<td>$\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{16}\text{O}</em>{27}$ or $\text{BaO} \cdot 2\text{MeO} \cdot 8\text{Fe}_2\text{O}_3$</td>
<td>M + S</td>
</tr>
<tr>
<td>Y</td>
<td>$2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{12}\text{O}</em>{22}$ or $2\text{MeO} \cdot 2\text{MeO} \cdot 6\text{Fe}_2\text{O}_3$</td>
<td>Y</td>
</tr>
<tr>
<td>Z</td>
<td>$3\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{24}\text{O}</em>{41}$ or $3\text{BaO} \cdot 2\text{MeO} \cdot 12\text{Fe}_2\text{O}_3$</td>
<td>M + Y</td>
</tr>
<tr>
<td>U</td>
<td>$4\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{36}\text{O}</em>{60}$ or $4\text{BaO} \cdot 2\text{MeO} \cdot 18\text{Fe}_2\text{O}_3$</td>
<td>2M + Y</td>
</tr>
<tr>
<td>X</td>
<td>$2\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{28}\text{O}</em>{46}$ or $2\text{BaO} \cdot 2\text{MeO} \cdot 14\text{Fe}_2\text{O}_3$</td>
<td>2M + S</td>
</tr>
</tbody>
</table>

Table 2.3 shows the different types of hexaferrites. Among these, S, M and Y-hexaferrites are fundamental and the combinations of these ferrites form other complex ferrites such as W, Z, U and X-hexaferrite. All these types are remarkably complex and interrelated to each other. The details about the crystal structure of few ferrites viz. M and Z-hexaferrites is discussed in Chapters 4 and 5, respectively.

Fig. 2.7: Chemical composition diagram for different types of hexaferrites

Table 2.3: Chemical relationship of hexaferrites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Interrelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$2\text{Me}^{2+} \cdot 2\text{Fe}_2\text{O}_4$ or $2\text{MeO} \cdot 2\text{Fe}_2\text{O}_3$</td>
<td>S</td>
</tr>
<tr>
<td>M</td>
<td>$\text{Ba}^{2+}2\text{Fe}<em>{12}\text{O}</em>{19}$ or $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$</td>
<td>M</td>
</tr>
<tr>
<td>W</td>
<td>$\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{16}\text{O}</em>{27}$ or $\text{BaO} \cdot 2\text{MeO} \cdot 8\text{Fe}_2\text{O}_3$</td>
<td>M + S</td>
</tr>
<tr>
<td>Y</td>
<td>$2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{12}\text{O}</em>{22}$ or $2\text{MeO} \cdot 2\text{MeO} \cdot 6\text{Fe}_2\text{O}_3$</td>
<td>Y</td>
</tr>
<tr>
<td>Z</td>
<td>$3\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{24}\text{O}</em>{41}$ or $3\text{BaO} \cdot 2\text{MeO} \cdot 12\text{Fe}_2\text{O}_3$</td>
<td>M + Y</td>
</tr>
<tr>
<td>U</td>
<td>$4\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{36}\text{O}</em>{60}$ or $4\text{BaO} \cdot 2\text{MeO} \cdot 18\text{Fe}_2\text{O}_3$</td>
<td>2M + Y</td>
</tr>
<tr>
<td>X</td>
<td>$2\text{Ba}^{2+}2\text{Me}^{2+}2^{+} \cdot 2\text{Fe}<em>{28}\text{O}</em>{46}$ or $2\text{BaO} \cdot 2\text{MeO} \cdot 14\text{Fe}_2\text{O}_3$</td>
<td>2M + S</td>
</tr>
</tbody>
</table>
Ferrimagnetism in Hexaferrites:

The origin of the ferrimagnetism in hexaferrites stems from the negative interaction present in the oxides, which is given by the theory of super-exchange interaction, first proposed by Kramers and later developed by Anderson. The superexchange interactions for Fe\(^{3+}\)-O-Fe\(^{3+}\) in hexaferrites are strong and negative, when the angle through the intervening oxygen ion is near 180°. Let us consider the oxygen ion labeled \(P\) and the three metal ions surrounding \(P\), as shown in Figure 2.8, where the angle Fe\(^{3+}(1)\)-O-Fe\(^{3+}(2)\) is 140° and Fe\(^{3+}(2)\)-O-Fe\(^{3+}(3)\) is 80°. Therefore, the superexchange interaction between Nos. 2 and 3 is negligible, and they both align anti-parallel to No. 1. Ion 3, in turn, coupled to the S\(_4\) block by the strong negative interaction Fe\(^{3+}(3)\)-O-Fe\(^{3+}(4)\). Therefore, the alignments of ions 3 and 4 are anti-parallel. In the latter case, it is the fact that the ions are so near to the intervening oxygen ion that is determining factor. The interaction Fe\(^{3+}(1)\)-O-Fe\(^{3+}(4)\) does not compete effectively because the distance of No. 1 from the intervening oxygen ion is 2.3 Å compared with a typical interaction distance of about 1.3 Å. The remaining alignments are also shown in Figure 2.8.

![Fig. 2.8: Superexchange interaction in barium hexaferrite for hexagonal \(B_1\) layer and the coupling to the cubic spinel layer](image)
The above description of super exchange interactions in the vicinity of the Me (Ba or Sr) layers account for the uni-axial anisotropy of hexaferrites. The uni-axial anisotropy gives material a *self-biased* property, which makes hexaferrites suitable for microwave applications. Further, since cubic spinel block has no strongly preferred axis of alignment, the coupling from the barium layer imposes its strong preferential orientation of the spinel block.

Each Fe$^{3+}$ ions contribute $5\mu_B$ (Bohr magnetons) to the magnetic moments at absolute zero, and we may form the algebraic sum of the contribution to determine the saturation magnetization. For example, in barium $M$-type hexaferrites (BaFe$_{12}$O$_{19}$), the twelve Fe$^{3+}$ ions of the formula unit consists of one ion in the $B_1$ layer (up) and two octahedral ions (down) and, in the $S_4$ block, seven octahedral ions (up) and two tetrahedral ions (down). The total is $5\mu_B \times (1-2+7-2) = 20\mu_B$, which is in excellent agreement with the experimental measurements of magnetization at very low temperatures.

**Bulk Resistivity:**
Apart from the magnetization and anisotropy property of these ferrites, another important property of the ferrites is their electrical resistivity, which makes them distinguishable from the ferromagnetic materials or alloys in compition. In these materials, the eddy-current losses in an alternating field of RF/microwave frequencies can be very low because of high volume resistivity$^{27}$. The resistivity of the ferrites is greater than the ferromagnetic metals. In ferrites, the presence of small amount of Fe$^{2+}$ amidst of Fe$^{3+}$ ions give rise to $n$-type conductivity if the temperature is high enough for the extra electron on the Fe$^{2+}$ ions to conduct through the crystal via hopping$^{28-29}$. This lowers the resistance of the material greatly. Therefore, in the preparation of ferrites for the electrical applications, it is necessary to prepare high resistivity ferrites by excluding the traces of Fe$^{2+}$ ions from the ferrites. This can be controlled during sintering process in the atmosphere ranging from pure O$_2$ to pure N$_2$, depending on ferrite composition and sintering temperature. Further discussion on these aspects is presented in the Subsection 2.8.2 of this Chapter.

**Magnetic anisotropy:**
Magnetic anisotropy is another important property of ferrites. Ferrites in the unmagnetized state consist of large number of small domains within which the material is magnetized to saturation. The direction of magnetization within domain takes up one of
the several preferred directions, resulting in the net magnetization to be zero. In contrast, when ferrites are magnetized, the direction of magnetization in any domain not initially in line with the magnetizing force will be rotated from its preferential directions. The ease with which this is achieved and consequently the forces involved in this anisotropy, will be reflected in the value of permeability\textsuperscript{30}. Thus, the magnetic anisotropy determines some of the important properties of ferrites such as susceptibility or permeability, resonance frequency, together with coercivity and remanent magnetization.

\textbf{Susceptibility/ Permeability\textsuperscript{29}:}

When the small field is applied in the direction perpendicular to the preferred direction, the magnetization $M$ rotates slightly into the field direction. The component of $M$ along the applied field divided by the value of the field is called the rotational susceptibility $\chi_r$. The quantity is given by:

$$\chi_r = \frac{M_s}{H_A}$$

(2.5)

where, $H_A$ is the anisotropy field.

A related quantity is the permeability $\mu$, which is given by,

$$\mu = 1 + 4\pi \chi_r$$

(2.6)

\textbf{Resonance frequency\textsuperscript{29}:}

In all ferromagnetic phenomena the value of magnetization plays an important part. In many cases a large value is required, preferably independent of temperature. Special requirements, however, have to be met in those cases where use is made of the gyromagnetic properties of a spin system. These properties are most pronounced for frequencies near the ferromagnetic resonance (FMR) frequency. This type of resonance is of the same nature as the nuclear, paramagnetic and anti-ferromagnetic resonance phenomena.

In order to understand the gyroscopic properties of a spin system it is important to realize that spins have both a magnetic moment, $M$, and an angular momentum $J$. The
ratio of $M/J$ is the gyromagnetic ratio, $\gamma$. The value of $\gamma$ is $\gamma = g(em/2c) = 1.76 \times 10^7$ rad/sec Oe for $g = 2$.

If a mechanical couple is exerted on the spin, e.g., by the action of a magnetic field $H$ on $M$, the direction of $J$ (and $M$) will be changed, according to the following equation of motion,

$$\frac{dj}{dt} = \frac{1}{\gamma} \frac{dM}{dt} M \times H$$  \hspace{1cm} (2.7)

From this equation the motion of $M$ is seen to be a precession around the direction of $H$. A magnetic field $h. e^{i\omega t}$ applied perpendicular to $H$ can excite this precession of $M$. The components of $M$ perpendicular to $H$ are related to $h$ by the equations

$$m_x = \chi_{xx} h_x + \chi_{xy} h_y$$ \hspace{1cm} (2.8)

$$m_y = -\chi_{yx} h_x + \chi_{yy} h_y$$ \hspace{1cm} (2.9)

The components of the $\chi$ tensor are given by,

$$\chi_{xx} = \chi_{yy} = \gamma^2 M_s H / (\omega_r^2 - \omega^2)$$ \hspace{1cm} (2.10)

$$\chi_{xy} = i\gamma M_s \omega / (\omega_r^2 - \omega^2)$$ \hspace{1cm} (2.11)

where, $H$ is the field inside the material and

$$\omega_r = \gamma H$$ \hspace{1cm} (2.12)

The factor $i$ in Eqn. 2.11 denotes a phase shift of 90 degrees between the component of magnetization parallel to $h$ and the transverse component. $\chi_{xx}$ is seen to show resonant behaviour when the exciting frequency $\omega$ equals $\omega_r$ as given by Eqn. 2.12.

The stiffness experienced by the spins when pointing in the preferred direction also influences the frequency of the ferromagnetic resonance. The resonant frequency is found to be increased from the value given by Eqn. 2.12. For example, if anisotropy constant $K_1 > 0$, and the magnetization pointing along[110]; the resonant frequency $\omega_r$, is given by,
\( \omega_r = \gamma (H + H_a) = \gamma (H + 2K_1 / M_s) \)  \tag{2.13}

Resonance can also be found without applying a d.c. field. Equation 2.13 then simplifies to,

\( \omega_r = \gamma H_a \)  \tag{2.14}

Such a situation is encountered in a measurement of the initial permeability. Since both \( \mu \) (or \( \chi \)) and \( \omega_r \) are determined by \( H_a \), the latter quantity may be eliminated by taking the product

\( \omega \chi (\omega = 0, \theta) = \gamma M_s \sin^2 \theta \)  \tag{2.15}

This relation is important because it shows that the use of high susceptibility materials, e.g. in a high quality inductor, is limited to angular frequencies below the value of \( \omega_r \), given by Eqn. 2.15, since otherwise the inevitable resonance loss spoils its properties. For a non-cubic material complications arise as the validity of Eqn. 2.13 may be violated. Such a case is encountered in hexagonal materials with a preferential plane of magnetization.

**Hysteresis and Remanence**

Anisotropy energy is also responsible for hysteresis. This is found when the applied field \( H \) is sufficiently large for the magnetization to rotate from one preferred direction into a different one that is nearer to \( H \). When the field is decreased, the magnetization describes a hysteresis loop. One of the characteristic quantities is the remanent magnetization for \( H = 0 \), usually expressed by the remanence ratio \( M_r / M_s \). The value of \( M_r / M_s \) is determined by the nature of the easy direction. In a uniaxial material the ratio is 0.5, in a cubic material with \( K_1 < 0 \) the value of \( M_r / M_s \) is 0.87, whereas for a planar material the ratio is only 0.06. In case no anisotropy is present, the \( M_r / M_s \) value vanishes and a straight line for \( M-H \) is observed.

Hysteresis loop has a second characteristic quantity, the value of the field where \( M = 0 \). The maximum possible value of this “coercive” field \( H_c \) is determined by the anisotropy. In practice, however, the value of \( H_c \) is often found to be lower than expected.
on the basis of a uniform magnetization and the value of $H_a$. The reason is that in real materials the magnetization is non-uniform, for example in Bloch walls.

2.5 Evaluation of Ferrites for Integrated Magnetic Components in LTCC

Ferrites cast as cofired tape and can be made compatible with LTCC process owing to their ceramic nature, much analogous to LTCC dielectric ceramics. In addition, ferrites have a long history as RF multilayer chip inductors (MLCI) and microwave materials. High performance MLCIs are available commercially and are widely used in substrate boards such as LTCC and PWB. The materials at the heart of the system of MLCI inductors are ferrites. With the advancement in low temperature synthesis of ferrites, the focus has now turned to integrate these materials with LTCC. It is thus imperative to provide a detailed account of ferrite based MLCI prepared using various substrates for RF applications.

2.5.1 Ferrites as/ for MLCI inductors

Ferrite based MLCI inductors have a long history for RF applications. Most chip inductors are optimized according to value and performance. These inductors are available within the range of 1 to 500 nH and find applications in mobile communication systems for VHF/ UHF circuits, GPS receiver systems, RF transceivers, RFID, WLAN etc. Table 2.4 compares the commercially available multilayer ferrite chip inductors for their inductance range, SRF and Q value.

<table>
<thead>
<tr>
<th>Table 2.4: Comparison of ferrite MLCIs</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Company</th>
<th>$L_{\text{eff}}$ (nH)</th>
<th>$Q_{\text{min.}}$</th>
<th>L &amp; Q Test Frequency (MHz)</th>
<th>SRF (MHz)</th>
<th>Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central Technologies</td>
<td>47</td>
<td>10</td>
<td>50</td>
<td>26</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>15</td>
<td>25</td>
<td>125</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>35</td>
<td>10</td>
<td>75</td>
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<td></td>
<td>33000</td>
<td>20</td>
<td>1</td>
<td>9</td>
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<td>Ferroxcube Int. Holding B.V.</td>
<td>47</td>
<td>20</td>
<td>50</td>
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<td>± 20 %</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>10000</td>
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<td>2</td>
<td>17</td>
<td>± 10 %</td>
</tr>
<tr>
<td>MLCI Supplier</td>
<td>Min. Core Size</td>
<td>Max. Core Size</td>
<td>Min. Inductance</td>
<td>Max. Inductance</td>
<td>Tolerance</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Fair-Rite Products Corp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 10 %</td>
</tr>
<tr>
<td>18000 30 1 18</td>
<td>± 10 %</td>
<td></td>
<td></td>
<td></td>
<td>± 10 %</td>
</tr>
<tr>
<td>15000 20 1</td>
<td>± 10 %</td>
<td></td>
<td></td>
<td></td>
<td>± 10 %</td>
</tr>
<tr>
<td>Chilisin Electronics Corp.</td>
<td>10 8 50 500</td>
<td></td>
<td>± 20 %</td>
<td>± 20 %</td>
<td></td>
</tr>
<tr>
<td>100 15 25</td>
<td>± 20 %</td>
<td></td>
<td>± 20 %</td>
<td>± 20 %</td>
<td></td>
</tr>
<tr>
<td>1000 20 10</td>
<td>± 20 %</td>
<td></td>
<td>± 20 %</td>
<td>± 20 %</td>
<td></td>
</tr>
<tr>
<td>2200 20 10</td>
<td>± 20 %</td>
<td></td>
<td>± 20 %</td>
<td>± 20 %</td>
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</tr>
<tr>
<td>Bourns Inc.</td>
<td>47 60 50 320</td>
<td></td>
<td>± 10 %</td>
<td>± 10 %</td>
<td></td>
</tr>
<tr>
<td>100 50 25</td>
<td>± 10 %</td>
<td></td>
<td>± 10 %</td>
<td>± 10 %</td>
<td></td>
</tr>
<tr>
<td>470 50 25</td>
<td>± 10 %</td>
<td></td>
<td>± 10 %</td>
<td>± 10 %</td>
<td></td>
</tr>
<tr>
<td>1000 80 10</td>
<td>± 10 %</td>
<td></td>
<td>± 10 %</td>
<td>± 10 %</td>
<td></td>
</tr>
</tbody>
</table>

(Sources: Company Website)

MLCIs are available in the standard sizes ranging from minimum $1.6 \times 0.8 \times 0.8$ mm to maximum $4.5 \times 3.2 \times 1.5$ mm. These inductors are soldered onto the substrate board by standard surface mount technology. MLCIs provide tremendous design advantage in contrast to their counterparts, ceramic MLCI, multilayer air core chip inductor and wire-wound air core chip inductors. The design advantages provided by MLCIs are:

- High resistivity - *useful for high frequency applications*
- Low loss combined with high permeability - *high inductance density*
- Large material selection - *wide range of inductance and operating frequency*
- Low dc resistance and high Q - *high performance characteristics*
- High reliability - *minimizes electromagnetic interference*
- Competitive in cost, weight
- Time and temperature stability

The combination of high resistivity and excellent magnetic properties of ferrite materials made them useful for various high frequency applications. The materials at the heart of these systems are soft ferrites with spinel crystal structure. Two major compositions of various oxides with iron oxide are used for the fabrication of MLCIs, Manganese-Zinc (MnZn) and Nickel-Zinc (NiZn) ferrite.
2.5.1.1 Manganese-Zinc (MnZn) ferrite

MnZn ferrites have high permeability and low eddy current losses than NiZn ferrite. These ferrites also found more applications than NiZn ferrite. The application decides the desirable material characteristics, which in turn determines the chemical composition of the MnZn ferrite. These ferrites are primarily used for frequencies less than 2 MHz. Figure 2.9 shows the composition diagram for MnZn ferrite with respect to optimum performance for saturation flux density ($B_s$), low losses ($Q$) and high initial permeability ($\mu_i$). The other variants of MnZn ferrites are MnMgZn and MnCuZn ferrites.

![Composition diagram for MnZn ferrite with respect to properties](image)

**Fig. 2.9:** Composition diagram for MnZn ferrite with respect to properties

2.5.1.2 Nickel-Zinc (NiZn) ferrite

This class of the soft ferrites is characterized by high resistivity, several orders of magnitude higher than MnZn ferrite. Owing to their high resistivity property, these ferrites are commonly used for high frequency applications, particularly above 1-2 MHz to several hundreds of mega hertz. The material is also characterized by high permeability and low losses, which is appropriate for their high frequency use. NiZn ferrites are also available with different substitutions to alter the magnetic properties and processing temperature so as to be useful for many applications, in much similar manner with MnZn ferrite. A summary of the typical MnZn and NiZn ferrite, indicating the major material parameter and operating frequency range, is outlined in Table 2.5.
Table 2.5: Summary showing range of properties for MnZn and NiZn ferrite as MLCI from commercial source

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MnZn ferrite</th>
<th>NiZn ferrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial permeability</td>
<td>1400 to 3500</td>
<td>750 to 3500</td>
</tr>
<tr>
<td>Curie temp. (°C)</td>
<td>180 to 280</td>
<td>150 to 250</td>
</tr>
<tr>
<td>Flux density (Gauss) @12.5 Oe</td>
<td>3500 to 5200*</td>
<td>2400 to 4750*</td>
</tr>
<tr>
<td>Typical operating frequency</td>
<td>10 to 500 kHz</td>
<td>150 to 250 kHz</td>
</tr>
<tr>
<td>Loss factor tanδ/μi×10^-6</td>
<td>10 @ 100 kHz</td>
<td>25 @ 1 MHz</td>
</tr>
</tbody>
</table>

The material chemistries for NiZn and MnZn ferrites with respect to their properties and their trade-offs are well known. Specific applications and technological trends drive the interests in materials development. For example, copper addition in NiZn ferrite reduces the sintering temperature of the material system below 950°C. Thus, as a result of low temperature sintering, NiCuZn ferrite has been incorporated in LTCC for more advanced applications, which is described in the Section 2.5.2 of this Chapter.

In conclusion, although the use of surface mount MLCIs is standard in today’s electronics, the future trends in the electronics will put limitations on using them in the modern electronics. The major limitations are due to technological advancement in miniaturization of electronic systems and their operating frequency range. New materials, designs and process technologies are needed to develop more advanced high frequency applications. With the availability of low temperature sintered MLCI such as NiCuZn ferrite, the possibility of integrating these materials with LTCC has renewed interest in developing more advanced applications. In general, LTCC offers tremendous advantages over present day MLCIs, which is outlined in Table 2.6.
Table 2.6: Advantages of LTCC over surface mount MLCIs

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Surface mount ferrite MLCIs</th>
<th>LTCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Larger footprint, bulky devices</td>
<td><strong>Proven miniaturization</strong> by integrating ferrite inductor in LTCC</td>
</tr>
<tr>
<td>Inductance</td>
<td>Low to high</td>
<td><strong>Offer low to high inductance</strong></td>
</tr>
<tr>
<td>SRF</td>
<td>Low for futuristic devices</td>
<td><strong>High SRF materials possible</strong></td>
</tr>
<tr>
<td>RF losses</td>
<td>Low</td>
<td><strong>Low loss materials possible</strong></td>
</tr>
<tr>
<td>Processing temp.</td>
<td>~ 900 -1000 °C</td>
<td><strong>Cofiring below 950 °C possible</strong></td>
</tr>
<tr>
<td>Performance</td>
<td>Satisfactory</td>
<td><strong>Offer better performance</strong></td>
</tr>
<tr>
<td>Speed</td>
<td>Slower than LTCC: larger distance between inductor and other devices</td>
<td><strong>May offer faster speed:</strong> inductor in close proximity with other devices</td>
</tr>
<tr>
<td>Reliability</td>
<td>Questionable vis-à-vis LTCC</td>
<td><strong>Better than MLCI:</strong> due to elimination of solder joints</td>
</tr>
<tr>
<td>Cost</td>
<td>Individually low cost due to mass production. Overall, high cost due to assembly processes and total no. of components</td>
<td><strong>Cost competitive</strong></td>
</tr>
</tbody>
</table>

LTCC technology offers the electronic package preparation process below 900 °C, *i.e.* the processing temperature must be below the melting temperature of commonly used conductors in LTCC (e.g. Ag, Au, AgPd and AuPt) to obtain assured reliability. Recently, many new low temperature sintering methods have been developed that allows incorporation of ferrites in LTCC technology, which are discussed in the following Section.

### 2.5.2 LTCC ferrites

The integration of ferrites into existing LTCC dielectrics would have a dramatic impact on miniaturization and the overall performance of the device in order to cater the tomorrow’s demand for faster, smaller and better electronics. RF inductors, antennas, transformers, circulators *etc.* are only some of many passive devices that could be realized if LTCC compatible ferrite tapes and other formats are made available. The development of ferrites in LTCC has a constraint of matching sintering temperature, thermal expansion coefficient and shrinkage with the host tapes. Another important aspect that needs to be considered while developing such materials is their possible diffusion and chemical interaction with each other during sintering. Clearly, the task of
ferrite materials development and compatible process technologies for LTCC is daunting.

Several new-techniques were developed to achieve defect-free LTCC structures when cofired with ferrites. Zero shrinkage and constrained sintering are some possible methods that could match the shrinkage of stand-alone tape systems\textsuperscript{33-34}. This technique is also useful to match shrinkage of dissimilar tape systems such as ferrite tape and LTCC dielectric tape. In the zero-shrinkage technology the substrate material is cofired within the layers of release tape, which also utilizes pressure during sintering. Another concept is based on constrained sacrificial layers that are laminated on both sides of the multilayer structure. The friction force between the LTCC layer and the non-sintering sacrificial layer suppress the in-plane shrinkage. In this way, Hagymási \textit{et al.} has opted a constrained sintering method to match in-plane shrinkage of the ferrite tape with LTCC dielectric tape\textsuperscript{35}. Generally, the LTCC dielectrics densify at a different temperature region than the ferrite tape. The dielectric tape must densify at low temperatures, where it is constrained by the non-sintering green ferrite tape. At higher temperatures, the ferrite tape densifies, but the shrinkage is inhibited by the already dense dielectric tape. Thereby, a self-constrained sintering is accomplished, because each tape acts as a constraining layer, beside its functional performance. However, such method could results in defected sintered composites. The defects in the sintered composites are cavitation in LTCC dielectrics, debonding crack and channel crack in ferrite layer which occurred due to stress effects during sintering (dissimilar shrinkage) and cooling cycles\textsuperscript{35}. In order to overcome this problem, the unique method is to allow the low temperature densification of ferrites along with LTCC dielectrics. Clearly, some work on the ferrite material development is necessary.

Commercially available LTCC dielectric tapes densifies at 850-900 °C. While, the well known NiZn ferrite densifies at temperature more than 1000°C in order to obtain highest permeability of the final product (\(\mu \sim 350\)). Densification of NiZn ferrite around 900°C decreases the permeability to around 200. In order to reduce the densification temperature close to LTCC sintering temperature, copper (Cu) is substituted in NiZn ferrite, which proved to be a novel approach to reduce the sintering temperature. The material system is termed as NiCuZn ferrite, which is also a well-known materials system for MLCI. In addition, bismuth oxide (Bi\textsubscript{2}O\textsubscript{3}), vanadium oxide (V\textsubscript{2}O\textsubscript{5}) and low-melting glasses were introduced in NiCuZn ferrite to reduce the sintering temperature for co-firing with conductor and LTCC dielectrics. The different additives form liquid
phases in grain boundaries to enhance densification. In this way, ferrite material systems were developed to integrate with LTCC.

Based on the above technique, new ferrite materials have been developed that allow cofiring with LTCC dielectrics and conductor material system. Some of these ferrite materials are made available in the form of tapes, while others are presently a topic of research only. These materials can be used as stand-alone systems or sandwiched between standard LTCC dielectric layers. All available reports on integration of ferrites and their applications are summarized in Table 2.7.
### Table 2.7: Reports on Applications of ferrite integrated in LTCC

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ferrite material</th>
<th>Sintering temp. (°C)</th>
<th>$\mu_r$ or Inductance</th>
<th>SRF (MHz)</th>
<th>Paper theme/Potential application</th>
<th>Application properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ESL 40010® (NiZn)</td>
<td>885</td>
<td>***</td>
<td>***</td>
<td>Power converter (high freq.-high current)</td>
<td>***</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>ESL 40011®</td>
<td>885</td>
<td>***</td>
<td>***</td>
<td>Power converter</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ESL 40012®</td>
<td>885</td>
<td>***</td>
<td>***</td>
<td>LF transformer</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ESL 40012®</td>
<td>900</td>
<td>***</td>
<td>***</td>
<td>Tunable antennas</td>
<td>610 MHz near 12 GHz; Tuning bandwidth 4 - 5 %</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>ESL 40010®</td>
<td>875</td>
<td>***</td>
<td>***</td>
<td>Solenoid transformer</td>
<td>20 × 20 × 1.24 (t) mm</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>ESL 40010®</td>
<td>875</td>
<td>20-200 μH</td>
<td>***</td>
<td>Power inductors</td>
<td>$t_{ferrite}$: 0.2 - 1.3 mm</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>ESL 40010®</td>
<td>875</td>
<td>***</td>
<td>***</td>
<td>Integrated inductors (70 nH)</td>
<td>up to 500 MHz</td>
<td>39</td>
</tr>
<tr>
<td>8</td>
<td>ESL 40010®</td>
<td>920</td>
<td>450 @ 10 MHz</td>
<td>***</td>
<td>Integrated transformer</td>
<td>for low power switching applications (250 kHz to 2 MHz); 5.0 × 7.5 × 15 mm</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>LSF400 ferrites</td>
<td>920</td>
<td>400</td>
<td>***</td>
<td>LC filters</td>
<td>$f_{cut-off}$ 10 MHz; &gt;25dB attenuation above 360 MHz</td>
<td>43</td>
</tr>
<tr>
<td>10</td>
<td>Ferro F180®</td>
<td>900</td>
<td>***</td>
<td>***</td>
<td>LTCC solenoid transformer</td>
<td>35 × 12 × 1.13 (t) mm</td>
<td>44</td>
</tr>
<tr>
<td>11</td>
<td>NiZn</td>
<td>900</td>
<td>600 @ 2.0 MHz</td>
<td>***</td>
<td>Integrated inductors</td>
<td>***</td>
<td>45</td>
</tr>
<tr>
<td>12</td>
<td>NiZn</td>
<td>900</td>
<td>230</td>
<td>***</td>
<td>Integrated inductors</td>
<td>5.7 μH up to 5 MHz</td>
<td>46</td>
</tr>
<tr>
<td>13</td>
<td>NiCuZn</td>
<td>900</td>
<td>800 @ 2.0 MHz</td>
<td>***</td>
<td>Integrated Power converter</td>
<td>***</td>
<td>47</td>
</tr>
<tr>
<td>14</td>
<td>NiCuZn</td>
<td>900</td>
<td>600</td>
<td>***</td>
<td>Power inductors</td>
<td>Q: 30 up to 1MHz; SMD (1 mm): LTCC (0.4 mm)</td>
<td>48</td>
</tr>
</tbody>
</table>

Chapter 2
<table>
<thead>
<tr>
<th></th>
<th>Material</th>
<th>Frequency</th>
<th>Inductance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>NiCuZn</td>
<td>875-950</td>
<td>213 @ 5 MHz</td>
<td>Materials compatibility study</td>
</tr>
<tr>
<td>20</td>
<td>NiCuZn</td>
<td>900</td>
<td>300 nH</td>
<td>Materials development</td>
</tr>
<tr>
<td>21</td>
<td>NiCuZn</td>
<td>875</td>
<td>521 @ 10 MHz</td>
<td>Integrated DC-DC converter</td>
</tr>
<tr>
<td>22</td>
<td>NiCuZn</td>
<td>920</td>
<td>***</td>
<td>Band-pass filter (Middle freq. 10 MHz)</td>
</tr>
<tr>
<td>23</td>
<td>BaFe12O19</td>
<td>900</td>
<td>***</td>
<td>Materials compatibility study</td>
</tr>
<tr>
<td>24</td>
<td>Ba(CoTi)2xFe12-2xO19</td>
<td>920</td>
<td>***</td>
<td>Low pass filters</td>
</tr>
<tr>
<td>25</td>
<td>Ba(CoTi)2xFe12-2xO19</td>
<td>900</td>
<td>13</td>
<td>up to 1 GHz</td>
</tr>
<tr>
<td>26</td>
<td>Ba(CoTi)2xFe12-2xO19</td>
<td>900</td>
<td>2.52 μH</td>
<td>Inductor material development</td>
</tr>
<tr>
<td>27</td>
<td>BaFe12O19 (possibly Co/Ti)</td>
<td>900</td>
<td>14-16 @ 100 MHz</td>
<td>Materials compatibility study</td>
</tr>
<tr>
<td>28</td>
<td>Ba(CoTi)2xFe12-2xO19</td>
<td>900</td>
<td>14-16 @ 100 MHz</td>
<td>Integrated inductors (2.45 μH)</td>
</tr>
<tr>
<td>29</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>Integrated microstrip junction circulators</td>
</tr>
<tr>
<td>30</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>Integrated transformer (5.0 × 7.5 × 15 mm)</td>
</tr>
<tr>
<td>31</td>
<td>4000 nH/mm²</td>
<td>***</td>
<td>***</td>
<td>Integrated Inductor (11.5 × 11.5 × 0.7 mm)</td>
</tr>
<tr>
<td>32</td>
<td>NiCoZn</td>
<td>900</td>
<td>6 -14 @100 MHz</td>
<td>&gt; 200 MHz</td>
</tr>
<tr>
<td>33</td>
<td>Ba3Co2Fe24O41</td>
<td>900</td>
<td>3 @ 1 GHz</td>
<td>&gt; 1 GHz</td>
</tr>
<tr>
<td>34</td>
<td>Ba3Co2Fe24O41</td>
<td>900</td>
<td>2.5 up to 1 GHz</td>
<td>Materials development &amp; compatibility study</td>
</tr>
<tr>
<td>35</td>
<td>Ba3Co1.4Fe24.6O41</td>
<td>900</td>
<td>5 @ 1 GHz</td>
<td>&gt; 1 GHz</td>
</tr>
</tbody>
</table>

*** details not reported
Although the passive integration is not a new technology, the integration of ferrites in LTCC has been a topic of research for last five-seven years. A limited number of archived value papers are available on the integration of ferrite materials with LTCC system. On the other hand, there is only a solitary tape system that is made available commercially from ESL Electro Science. The tapes available from ESL are proprietary ferrite tapes with permeability 50, 200 and 500 for the LTCC ferrite tape number 40010, 40011 and 40012, respectively. From Table 2.7, it is clear that NiCuZn ferrite is the most explored material system for the integration with LTCC, mainly due to its low temperature densification (~900°C) capability. As described earlier in this Section, the Cu substitution promotes the low temperature sintering. Further, the densification at temperature around 900°C is enhanced by the use of well-known low temperature sintering aids such as Bi₂O₃ or low melting reactive BBSZ glass (Bi₂O₃-B₂O₃-SiO₂-ZnO glass) which is widely used in LTCC. As a result, NiCuZn ferrites can be integrated in LTCC to fabricate many magnetic devices. The advantage of using ferrites in LTCC is clear from Example 18 given in Table 2.7. It is seen that LTCC allows more than 50% reduction in the size of inductor if compared with its SMD MLCI counterpart. Thus, LTCC is seen as a best option for a realistic miniaturization of electronic modules required for modern electronics. Furthermore, the inductance values realized in ferrite LTCC inductors are in the range from nanohenries to the hundreds of microhenries, thus allowing signal and power electronic applications. LTCC integrated inductors found applications in power electronic applications which utilizes maximum frequency of operation in the range kHz to 1-2 MHz. On the other hand, these inductors also allow signal electronic applications in the frequency range below 10-20 MHz, as clear from the Table 2.7. This put limitations on the use of NiCuZn ferrite in higher frequency applications, while it signifies that integration of ferrite brings realistic miniaturization of the electronic components. Thus, in order to cater the demand for higher frequency integrated inductors for future electronics, there is a need for the new materials with resonance frequency well above 50-200 MHz.

The other explored ferrites for LTCC are M-type barium hexaferrite, Z-hexaferrite and NiCoZn spinel ferrite. It is seen from the Table 2.7 that these ferrite materials may overcome the limitations in frequency of operations posed by NiCuZn ferrites in LTCC. NiCoZn spinel ferrite is soft ferrite material which can be integrated in LTCC. The material allows resonance frequency above 200 MHz, which is suitable for high frequency applications. Further, Barium hexaferrite if doped with Co²⁺ and Ti⁴⁺ induces planar
anisotropy, which resulted in increase in the permeability of the material. The self-resonance frequency for these materials increases up to 1 GHz, which depends on the stoichiometric variation. These inductors provide high inductance density, high resonance frequency vis-à-vis their MLCI counterparts (cf. Table 2.2 with corresponding footprints as given in the text and Example 26, 28 of Table 2.7). Thus, these materials can be used for miniaturized 'high frequency' applications of integrated inductors in LTCC, as shown in the Example 24 to 28. The other type of hexaferrite i.e. Z-hexaferrite can also be used in the same way as it also allows higher resonance frequency outlined in the corresponding table. Transformers, various filters and micro-strip junction circulators are few more applications that have been integrated in LTCC, which only signifies the prospect of using ferrite with LTCC for miniaturized RF/microwave applications.

In conclusion, the material properties of the ferrites vary widely as a function of frequency; hence, the type of the component in which ferrite is used depends largely on the intended application. Another criterion for selecting ferrites is their sintering temperature, which allows their use in LTCC technology. Given the applications of high frequency integrated inductors and non-reciprocal devices for future electronics, the NiCuZn ferrite possess serious limitations on their use. Therefore, there is a need to select the appropriate ferrite materials from the vast array of ferrites that are compatible with LTCC process technology. Simultaneously, the high performance ferrites for advanced magnetic components must be selected from the viewpoints of futuristic need of the modern electronics. The selection criteria of the ferrites are discussed in the following Section, which allows selection of ferrite materials for integration in LTCC for improved performance.

2.6 Selection of Ferrites for Their Integration with LTCC

Although there are numerous ferrite materials and their applications are available, the work presented in the thesis contains ferrite materials development for integrated inductors and non-reciprocal devices in LTCC for high frequency applications. The underlining aspect of this work is the development of ferrites for high performance integrated devices. For example, inductors require a smaller size and higher self resonant frequency to satisfy the soaring need of the modern electronics, so the inductance density and SRF becomes important while designing or choosing the inductor material.
Similarly, for non-reciprocal devices, they must be integrated from their presently available bulky and stand-alone/drop-in form. The need for improvement for these devices can best be judged from the technology roadmap. The possible roadmap for integrated magnetic components in LTCC, specifically integrated inductors and integrated non-reciprocal devices, are outlined in Table 2.8.

**Table 2.8: Technology roadmap for integrated magnetic components**

<table>
<thead>
<tr>
<th>Device</th>
<th>Enabling attribute</th>
<th>Presently available</th>
<th>Roadmap</th>
<th>Proposed solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inductor</strong></td>
<td>Size</td>
<td>Bigger SMD &amp; integrated inductors</td>
<td>Integrated inductor</td>
<td>Integration in LTCC</td>
</tr>
<tr>
<td></td>
<td>Inductance density for integrated inductor</td>
<td>Low inductance density for integrate inductors</td>
<td>High</td>
<td>Soft / hard ferrites in LTCC</td>
</tr>
<tr>
<td></td>
<td>Processing temperature</td>
<td>≥ 950 - 1000 °C</td>
<td>≤ 900 °C</td>
<td>New synthesis approach and use of sintering aids</td>
</tr>
<tr>
<td></td>
<td>SRF</td>
<td>below 200 MHz</td>
<td>SRF above 200 MHz</td>
<td>New materials amenable to UHF/VHF frequencies</td>
</tr>
<tr>
<td></td>
<td>Materials</td>
<td>NiCuZn/ MnZn ferrites etc.</td>
<td>××××</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tolerance</td>
<td>± 10-20% in SMD inductors</td>
<td>Better than ± 10-20%</td>
<td>New materials, design and processes required</td>
</tr>
<tr>
<td><strong>Non-reciprocal devices</strong></td>
<td>Size</td>
<td>Larger and bulky</td>
<td>Smaller &amp; Integrated</td>
<td>Integration in LTCC</td>
</tr>
<tr>
<td></td>
<td>Materials</td>
<td>Hard ferrites</td>
<td>Self-biased materials</td>
<td>Hard ferrites in LTCC; e.g. BaFe12O19</td>
</tr>
<tr>
<td></td>
<td>Processing temperature</td>
<td>≥ 1200 °C</td>
<td>≤ 900 °C</td>
<td>New synthesis approach and use of sintering aids</td>
</tr>
</tbody>
</table>

In order to survive the challenges posed by the modern electronics, the need of the hour is to develop the new materials which expand the performance and reduce the tolerance window. Choice of one single optimum ferrite material for every application is not possible. The selection of the ferrite materials can be made based on the property of the intended application. Ferrite materials can operate below or above natural resonance, as low loss and high permeable materials are required for the devices such as inductors, filters, phase shifters, circulators and isolators. Above resonance condition, inductor no more behaves as inductor and works as capacitor. Similarly, ferrites operate near natural resonance for their use as absorber or electromagnetic interference shielding materials. This signifies that permeability (magnetization), loss-factor and self resonant frequency are primary enabling attributes of the material selection for the ap-
plications envisioned in the thesis. Thus, the material selection for the LTCC integrated high performance magnetic components is presented in Table 2.9, with respect to their underlining properties for integrated inductor and non-reciprocal devices.

Table 2.9: Comparison of ferrites for integration with LTCC

<table>
<thead>
<tr>
<th>Ferrite types</th>
<th>Ferrite materials</th>
<th>Magnetization $4\pi M_s$(Gauss)</th>
<th>Gyromagnetic resonance $f$(GHz)</th>
<th>Key points to skip/ select ferrites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>YIG</td>
<td>1700</td>
<td>1-36</td>
<td>• Low $4\pi M_s$, although low losses</td>
</tr>
<tr>
<td></td>
<td>YFeAl</td>
<td>400-1700</td>
<td>1-6</td>
<td>• High processing temperature</td>
</tr>
<tr>
<td></td>
<td>YFeGd</td>
<td>1000</td>
<td>1-10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>YFeCaV</td>
<td>1000-2000</td>
<td>1.5-10</td>
<td></td>
</tr>
<tr>
<td>Spinel</td>
<td>MnZn</td>
<td>4000</td>
<td>---</td>
<td>• High $4\pi M_s$</td>
</tr>
<tr>
<td></td>
<td>MgMn</td>
<td>1200-2800</td>
<td>7-15</td>
<td>• Low resistivity</td>
</tr>
<tr>
<td></td>
<td>NiAl</td>
<td>500</td>
<td>1-6</td>
<td>• Low SRF</td>
</tr>
<tr>
<td></td>
<td>Li ferrite</td>
<td>3500-5000</td>
<td>1-30</td>
<td>• High SRF and $4\pi M_s$</td>
</tr>
<tr>
<td></td>
<td>NiZn</td>
<td>3200-5000</td>
<td>5-40</td>
<td>• Very high processing temperature</td>
</tr>
<tr>
<td></td>
<td>NiCo</td>
<td>1800-3000</td>
<td>0.5-10</td>
<td>• High SRF and $4\pi M_s$</td>
</tr>
<tr>
<td>Hexa-ferrites</td>
<td>M, W, Y, Z – type</td>
<td>4500</td>
<td>1-100</td>
<td>• High SRF and $4\pi M_s$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Low loss materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Relatively low processing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>temperature for $M$- and $Z$-type</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>hexaferrite</td>
</tr>
</tbody>
</table>

Based on the literature survey presented in Table 2.7 and Table 2.9, it is seen that cobalt substituted NiZn ferrite and M&Z-hexaferrite materials can fulfill the soaring demands of high inductance, high SRF value materials required for modern electronics. Simultaneously, these materials can be integrated in LTCC, however, there is a need to lower the sintering temperature of these materials close to LTCC sintering temperature, while retaining its necessary properties.

2.7 Summary of the Magnetic Properties of Ferrites and Their use in LTCC

Ferrites play an important role in power electronics and high-frequency telecommunications in the frequency range from $10^3$ to $10^{11}$ Hz. Different types of ferrites such as, spinel ferrites, hexaferrites, and garnets have been explored for various applications.
The uncompensated spin of these materials offer many remarkable properties, which makes ferrite especially useful for high frequency applications in comparison to other magnetic materials. The properties are:

- The resistivity of ferrites is higher than that of ferromagnetic metals which makes it useful to reduce eddy current losses in an alternating field of high frequency
- Available with wide range of saturation magnetization ($4\pi M_s$), typically 300 to 5000 Gauss
- Moderately high permeabilities available; $\mu Q$ product higher than other materials
- Ferrites with their gyromagnetic behaviour may be used to realize the non-reciprocal devices. They exhibit ferromagnetic resonance property, i.e. the electromagnetic energy absorption that is a function of internal static magnetic field useful to devise many applications
- Offer intrinsic anisotropy, to devise both non-reciprocal and inductor-like applications
- Good control over magnetic properties by adapting substituted ferrites
- Excellent tuning of hysteresis loop properties to devise intended applications
- Low dielectric losses
- Excellent stability over temperature, time, a.c. flux density, d.c. bias etc.
- Cost much lower than ferromagnetic alloys and thin tapes
- Good wear resistance
- Easily adapted to mass production
- Ease of forming shapes

The selection of the ferrites for LTCC involves trade-offs of one or more parameters. Based on the discussions performed in this and preceding Sections, the selection of ferrite materials for integrated magnetic components in LTCC can be made from the viewpoints of ferrites for two main applications intended in this thesis, i.e. integrated inductors and integrated non-reciprocal devices.
**Materials for Integrated inductors in LTCC:**

- NiZn ferrite is the most suitable and versatile material for inductor applications. Further, the NiZn ferrite is well proven for its use as MLCI material. (cf. Table 2.5, 2.7)

- Cobalt (Co) based ferrite have high gyromagnetic resonance frequency. Therefore, Co substitution in NiZn ferrite can be a best option for VHF band integrated inductors.

- Z-hexaferrites have high gyromagnetic resonance frequency and low loss material. The material can be used as UHF band inductor owing to high self-resonance frequency. (cf. Table 2.7, 2.9)

**Materials for Integrated non-reciprocal devices in LTCC:**

- Hexaferrites are suitable for non-reciprocal application, as these applications are based on the self-biased property of the material to control the microwave signal properties. In this respect, M-hexaferrite is suitable candidate owing to its high intrinsic anisotropy along with high magnetization. Barium hexaferrite, BaFe₁₂O₁₉ is one of the well-proven materials for non-reciprocal applications. The material exhibits high magnetization and low sintering temperature in contrast to Strontium hexaferrite, other material system from M-hexaferrite family.

If these materials are to be integrated in LTCC, they must exhibit sintering below 900 °C. For optimum magnetic properties of NiZn ferrite, M and Z-type hexaferrites, the sintering temperature of these materials are well above 1000°C, which hinders their use in LTCC. However, there are ample reports on low temperature synthesis and sintering of these ferrites, which allow their integration with LTCC. The utility of these materials in LTCC finally depends upon their processing temperature. Synthesis of ferrites is an enabling attribute that governs their processing temperature and the materials properties. This part of the thesis is present in the next Section.

### 2.8 Synthesis of Ferrites

Ferrites are ferrimagnetic ceramics that are used at both radio and microwave frequencies. In ferrites, one is principally concerned about the phenomenon of ferrimagnetism
which starts from the arrangement of atoms on particular crystallographic sites in a unit cell. It gives resultant macroscopic magnetic properties of a crystallite, which also introduces the concept of domains. This leads to a well-known phenomenon of hysteresis which has a particular importance in various RF/microwave applications. Besides these basic magnetic properties, the permeability and resistivity are of equal importance when designing the magnetic devices. All these properties, suitable for high frequency applications are primarily obtained from fine grained, defect-free and porosity-free sintered structures. However, the basic magnetic properties as well as the physical structure of the ferrites are influenced considerably by the processing techniques and conditions adopted. Therefore, synthesis and processing strategies of ferrites play an all important role in devising high performance applications.

The goal common to all the ferrites is the formation of single phase compound with desired crystal structure, stoichiometry and the valency of the iron ion. These requirements can be met by carefully controlling two processing steps:

1. Powder preparation
2. Sintering

These steps are quite closely intertwined. The characteristics of the powder will strongly affect the quality of the product after sintering. Any inadequacies in the powder can be corrected by sintering the ferrites at elevated temperatures for prolonged time, but usually at the cost of deterioration of other properties.

2.8.1 Powder Preparation

Ferrites can be prepared by almost all the existing techniques of solid state chemistry, leading to a wide variety of form: polycrystalline or single crystal powder. Among these, the single crystal ferrite preparation involves specialized preparation process, which is often a costly affair. Therefore, the use of single crystal is shunned for most of the applications, even though these materials exhibit better properties than the polycrystalline counterparts. The single crystal preparation techniques are, therefore, not the subject of discussion in this thesis. In contrast, polycrystalline ferrites are used in virtually every application and they are also available commercially. Polycrystalline ferrites are prepared by both solid state reaction and chemical synthesis route. These are discussed below in brief.
2.8.1.1 Solid-state reaction and calcination

Solid state reaction is a conventional technique and chosen commercially over all available techniques due to simpler, faster and cost-effective nature. There are two alternatives for this technique. One, solid oxide method, and the other being thermal decomposition method. Both methods are similar in nature. In thermal decomposition, salts of carbonates, nitrates or oxalates are mixed, milled in the desired proportion, and then pre-heated (called calcination) to obtain oxides by thermal decomposition. On the other hand, solid oxide method utilizes constituent oxides in the desired stoichiometry, and then mixed, milled and pre-heated at 700 to 1400 °C for several hours to obtain the desired ferrite composition. Typically, the calcination temperature required for spinel ferrite is 700 to 1200 °C, whereas, hexagonal ferrite requires calcination temperature above 1200 °C to obtain optimum properties required for high frequency applications. After calcination, agglomerated powder must be milled again to obtain homogenized composition with uniform and small particle size. Large variation in the particle size is avoided as they can nucleate non-uniform grain growth during sintering and deteriorate the magnetic properties. This step is called sieving, followed by granulation of the powder with mixing number of organic binders to form the powder in required shapes. The shapes are either in the form of pellets (circular, toroidal or any other) or slip cast, as required for the LTCC technology. These ferrite forms are then subject to sintering, again at elevated temperature of 1000 to 1400 °C for several hours to obtain dense and defect free ferrites. The sintering of the ferrite is discussed in more details in the Section 2.8.2.

Solid-oxide technique, although preferable in most cases, have some disadvantage. The major disadvantage comes with very high temperature processing, which results in cost escalation and not so user/environment friendly process. Despite this fact, the technique simultaneously offers mass production which compensates the cost of the ferrite device. However, the ferrite product as-obtained from this step usually have loose tolerance and magnetic properties of the ferrite components, which is useful for applications other than high frequency and high-end electronics. The underlining reason lies in the principle of solid state reaction, which utilizes high temperature processing. The high temperature processing allows initial size of the particles in the tens of microns, which upon sintering resulted in non-uniform grain growth of the sintered ferrites. This significantly affects one or more of the critical magnetic properties, which limits the
overall performance of the devices. Grain growth during sintering can be better controlled if the initial size is small and uniform\textsuperscript{67}. This can be obtained by repeated ball/attritor milling (\textit{i.e.} pulverization), however, again limiting the performance due to contaminants in the final product. The alternative is to adopt novel chemical synthesis routes, which results in small and uniform size of the starting ferrite powder, which is discussed in the next section.

For more details on the solid-state techniques for the formation of ferrites, one should refer to the classic ferrite text books, as virtually every textbook provides equal insights into the subject. The following ferrite textbooks have been referred here: \textit{Magnetic Ceramics}\textsuperscript{67}, \textit{High Frequency Applications of the Ferrites}\textsuperscript{30}, \textit{Ferrite: An Introduction to Microwave Engineers}\textsuperscript{68} and \textit{Microwave Ferrites}\textsuperscript{24}.

\subsection{2.8.1.2 Chemical synthesis routes}

Scientific advances in developing and understanding novel chemical synthesis techniques began in the 1970s - 1980s, and still remain the areas in need of research attention. There is vast number of archived value research publications, review articles and even books that outlines the advancements of various chemical techniques\textsuperscript{28,69-72}. Numerous chemical methods can be used to synthesize ferrites: combustion, co-precipitation, glass crystallization, hydrothermal, micro-emulsion, polyol, sol-gel, spray-drying, thermolysis, water-in-oil emulsion \textit{etc}. Most of these techniques offer uniform distribution of the fine ferrite powders of the size 10-200 nm and provides compositional homogeneity, good magnetic properties, ease in the synthesis and economic process. The precursor powder formed by these methods often need to be heat-treated to obtain the ferrimagnetic properties. The synthesis and processing conditions can easily allow formation of spinel ferrite below 1200 °C without any unwanted phase. On the other hand, formation of hexaferrite is an extremely complicated process because it often decomposes to other phases upon heat-treatment\textsuperscript{28}. When the precursor powders of M/ Z-hexaferrite are heat-treated, the unwanted major/minor phases, such as, \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, \(Y\)-hexaferrite phase and \(W\)-type hexaferrite phase exist if heat-treated below 1200 °C. Therefore, these ferrites require temperature above 1200-1300 °C to obtain single phase compound with optimum magnetic properties. Such high temperature processing is economically not favourable. Combustion synthesis, on the other hand, allow very high local temperature (>2000 °C) for short period of time during
combustion. Due to this inherent advantage of combustion synthesis, ferrites, such as, $M$ or $Z$-hexaferrites can easily be formed with calcination temperature below 1200 °C without any unwanted phase. The method also allows fine production of particles in the range 10 nm or above. Therefore, the combustion synthesis has been chosen over all other techniques in view of the formation of intended $M$ and $Z$-hexaferrites for this work. The same technique has been adopted for the formation of intended spinel ferrites. The other attributes of synthesis techniques are:

**Attributes of combustion synthesis route are:**

- Fast formation of the ferrite particles, usually within seconds after evaporation of water in the precursor solution
- Temporal very high local temperature (> 2000 °C)
- Economically attractive and easy to scale-up
  
  Formation of virtually any size (nano to micron) and any shape (spherical to hexagonal; some of the available technique allows hierarchy in the particle shapes which is advantageous not observed in case of combustion synthesis)

**The combined attributes of other chemical synthesis routes are:**

- Preparation of uniform and fine particle ferrites of size 10 - 600 nm
- Easy, fast and cost-effective route
- Assured composition, structure, homogeneity and stoichiometry of the ferrite

A typical combustion synthesis is discussed below.

**Combustion synthesis:**

Combustion synthesis for the preparation of fine particles makes use of the strong exothermic redox reaction between oxidant and fuels. The precursor slats of oxidants are usually metal nitrates, while fuels could be tetraformaltrisazine (TFTA), oxalic acid dihydrazine (ODH), glycine *etc*. In the typical process, stoichiometric ration of nitrates are dissolved in the minimum amount of water, and the fuel is added. Finally, the resultant solution is heated at 350 °C in oven/ muffle furnace. Self-propagating combustion then takes place after evaporation of water and finally, a ferrite precursor is obtained within few seconds. The method has been used for the synthesis of hexaferrites, garnets.
and a variety of spinel ferrites. The observed particle size for these ferrites is in the range of 20-600 nm for different experimental conditions. The synthesis also allows uniform distribution of ferrite powders. A typical process flow for the combustion synthesis is shown in Figure 2.10.

![Diagram of combustion synthesis process]

**Fig 2.10:** Typical combustion Synthesis process

For more theoretical and experimental aspects of the combustion synthesis, the textbook by K. C. Patil *et al.*[^69] can be referred.

### 2.8.2 Sintering

Once the precursor ferrite powder is made, the next step is sintering of the ferrites at temperatures between 1000 to 1400 °C for 2-24 hours. During sintering, there is a tendency for most ferrites to let off oxygen, as the equilibrium pressure in the reaction is often greater than one atmosphere and increases rapidly with temperature. This gives rise to the formation of ferrous ions due to oxygen deficiency in the final product[^24]. It is

[^69]: Patil, K. C. *et al.*
[^24]:
well-theorized that ferrous ions significantly affects the resistivity and causes increase in the dielectric and magnetic loss of the ferrites, which is undesirable for RF/microwave applications. Therefore, the sintering is done in atmosphere ranging from pure O\textsubscript{2} to pure N\textsubscript{2}, depending on ferrite composition and sintering temperature. The sintering step is all important in two respects for this thesis. One, the sintering of the ferrites gives possible porous-free, fine grained and defect-free final product. While, it is a prerequisite for this work is to sinter the ferrites around 900 °C so as to useful in conjunction with LTCC dielectrics. Both the methodologies are discussed below.

Since ferrites possess very high melting temperature, both reaction and densification usually taken place in the solid state. For densification of the ferrite bodies, the well-known method is induce liquid phase sintering that allows densification at much lower temperature than normal calcination or sintering temperature. The liquid phase sintering can be induced in the ferrite matrix by low temperature sintering aids, such as, Bi\textsubscript{2}O\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, B\textsubscript{2}O\textsubscript{3}, PbO-WO\textsubscript{3} etc, or by the low-melting glasses such as BBSZ glass (Bi\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-ZnO). During liquid phase sintering of these sintering aids, as reaction proceeds, there is a grain growth mechanism of the ferrite particles that increases the length of the diffusion paths of the reactants and thus decreasing the reaction rate. The main diffusion mechanism at this stage is volume (or bulk) diffusion, which depends on the point defect of the solid. This way more homogeneous products can be obtained. Reaction rates depend on the particular composition takes place during sintering as well as the process of elimination of the voids, or porosity, between the particles in the green body, leading to an dense ferrites\textsuperscript{67}. The initial particle size is critical, since the driving force for the sintering is the reduction in the surface free energy of the powder. A small particle size of the reactant powders provides a high contact surface area for initiation of the solid state reaction; diffusion paths are shorter, leading to more efficient completion of the reaction. Porosity is easily eliminated if the initial pores are very small. A narrow size distribution of the spherical particles as well as their dispersed state is important for compaction of the powder during green body formation. Grain growth during sintering can better be controlled if the initial size is small and uniform\textsuperscript{67}.

Prior to sintering, the ferrite powders are subjected to sieving and pulverization followed by green compaction either in the form of pellet or slip cast. Organic binders are used for the green compaction in the desired pellet form, which subsequently burns-off during sintering. The other shape forming conditions are thick-film printing or slip casting. Thick-film printing of the ferrites is employed in the thesis to study the com-
patibility of ferrites with LTCC, which is discussed in the Chapter 6. After desired shape formation, the pellets/thick-films are subject to sintering as discussed earlier.

In this Thesis, while considering all advantages and disadvantages of the ferrite preparation routes, solid-state reaction containing high-purity oxides is employed in the preparation of NiCoZn spinel ferrites due to relatively low processing temperature \textit{i.e.} below 1200 °C. It is also understood from the thorough literature review that high permeability and high quality materials, the purity of the starting powder should be very high. Simultaneously, the spinel ferrite is prepared by solution combustion synthesis is employed to synthesize fine and uniform distribution of NiCoZn spinel ferrite. The technique allows low temperature preparation of the particles \textit{i.e.} at 350 °C, followed by calcination and sintering at temperatures lower than 1000 °C. While, in case of hexaferrites (\textit{i.e.} \(M\) and \(Z\)-hexaferrites), it is understood that the conventional oxide route of these ferrite requires formation temperature above 1200-1300 °C. Therefore, solution combustion synthesis alone has employed as an alternative to conventional oxide route. Further, the combustion synthesis allows small and uniform size distribution of the initial ferrite precursor, which may be useful in controlling the grain growth appropriate for the best sintered product. This advantage is difficult to realize in solid state reactions. Subsequently, all chosen ferrites are subjected to form shaping followed by sintering with or without the help of the sintering aid. The sintering aids used in the study are well-known low temperature liquid phase sintering aids such as \(\text{Bi}_2\text{O}_3\) and low-melting reactive glass such as BBSZ glass, which are well-known for their use in LTCC as described earlier.

After synthesis/processing of ferrites, the next step is to study its magnetic, physical, structural and chemical properties. The studies on deterioration or superiority of these properties allow researchers to optimize the synthesis and processing conditions set-up for the preparation ferrites. This also allows the evaluation and the utility of the synthesized ferrite material for the intended application. Therefore, appropriate characterization is indispensable for the development of ferrites. The characterization techniques employed in this work are discussed in the following Section.
2.9 Characterization of Ferrites

Development of ferrites involves several key steps. Besides modeling (theory) and synthesis (experimental) of the material, the characterization is also indispensable, from scientific composition-structure-property relation to technological performance-quality-reliability assessment, during various stages of ferrite materials and device developments. The study presented in this thesis mainly involves structural-spectroscopic characterization and magnetic measurements aiming at scientific, while, electrical characterization at application level. A section of this chapter, thus concentrates on a compilation of these techniques and related scientific approach employed in this work to extract the structure-property data and technological performance of the synthesized material. The following sub-Sections are confined to a concise discussion on particular aspects of the characterization method carried out in the thesis. For more details on the technique and their instrumentation, one should refer to the excellent textbooks as indicated in the sub-Sections.

2.9.1 Structural and Elemental Characterization

The sub-section includes diffraction, microscopic and spectroscopic methods to understand the atom arrangement, structural order, defects, impurities, morphological aspects and elemental analysis etc. of the synthesized ferrite material. These techniques differ in their capability to probe the material at different resolution according to the extent of their excitation wavelength. A brief and point-wise discussion is presented in the following sub-sections from the viewpoints of extent of capabilities (capabilities of characterization) used in the Thesis. The section also covers a brief introduction on the instrumentation used in the Thesis.

2.9.1.1 X-ray Powder Diffraction

The synthesized ferrite materials if annealed at elevated temperature with a dwell time results in polycrystalline bulk material. The identification of the material or more particularly, the identification of the crystalline phases in these materials is routinely possible with X-ray powder diffraction (XRD) technique. In general, when a collimated
monochromatic beam of X-radiation incident on polycrystalline material, diffraction takes place according to the Bragg’s law:

\[ 2d_{hkl}\sin\theta_{hkl} = n\lambda \]  

(2.16)

where, \(d_{hkl}\) is the d-spacing between \((hkl)\) plane and \(\theta_{hkl}\) is the angle between the atomic planes and the incident (and diffracted) X-ray beam. The diffraction pattern produced by the above condition can act as unique fingerprint for the phase of particular material. Owing to the huge database managed by Joint Committee on Powder Diffraction Standards (JCPDS) and Crystallography Open Database (COD), the pattern-recognition can be possible by manual technique or computer based algorithm. This technique covers various investigations, including identification of crystalline phases and unwanted impurities, determination of lattice-parameter identification of lattice-type and reflection conditions etc. Besides the available data bank, the indexing of the pattern and calculation of lattice parameter for the synthesized cubic and hexagonal ferrite material can be done by mathematical as well as analytical method described in the textbook by Cullity. Further, the crystallite size was estimated using Scherrer formula from the line broadening of the strongest diffraction peak. From Scherrer formula:

\[ D = \frac{K\lambda}{B\cos\theta} \]  

(2.17)

where, \(K = 0.9\) is the shape factor for spherical crystallite, \(\lambda\) is the excitation wavelength, \(B\) is the line broadening at half the maximum intensity (FWHM) in radians and \(\theta\) is the Bragg angle and \(D\) is the crystallite size, smaller or equal to the grain size. Understanding these effects together with the acquired information on lattice is important in allowing the correct interpretation of the synthesized material. For more extensive information, a textbook by B. D. Cullity can be referred.

### 2.9.1.2 Mössbauer Spectroscopy

The Mössbauer effect, commonly known as Mössbauer spectroscopy, is the most powerful tool to probe the magnetic structure of the ferrite. The Mössbauer spectroscopy in this study relies on the fact that \(^{57}\text{Fe}\) (a decay product of \(^{57}\text{Co}\)) observes the nuclear \(\gamma\)-
ray fluorescence using the recoil-free transitions of a nucleus embedded in solid lattice. Here, we probe the 14.4 keV transitions \( \frac{3}{2} \rightarrow \frac{1}{2} \) by observing a count rate as a function of the relative velocity between the suitable \( \gamma \)-ray source and an absorber by Doppler motion. The spectra thus consist of relative counts versus relative velocity plots. Figure 2.11 presents the formation of sextets in bulk ferrites by Zeeman splitting and electric quadrupole interaction.

![Energy level diagram](image)

**Fig. 2.11:** Energy level diagram of \(^{57}\text{Fe}\), 14.4 keV transitions \( \frac{3}{2} \rightarrow \frac{1}{2} \), first-order quadrupole perturbation on a magnetic hyperfine spectrum

The typical Mössbauer spectra carries information about the amount of resonant absorption, line pattern characteristic of various phases, isomer shift, and line splitting caused by nuclear hyperfine interactions, *etc*, which is used to provide insight into the local atomic environment of atoms responsible for resonance. The physical phenomena contribute to these parameters are discussed below.

When the source and absorber atoms are in different chemical environment, the difference in the \( s \)-electron density causes the isomer shift (\( \delta \)). This leads to electric monopole interaction, altering the nuclear energy levels. Any difference in the \( s \)-electron density produces a shift in the resonance energy of the transitions. Graphically, it is the difference between the midpoint of the doublet and zero on the velocity scale.
The magnitude of the isomer shift gives information about the oxidation state of Fe nucleus, coordination environment, the symmetry of the site etc. For example, the presence of ferrous or ferric ions in the synthesized ferrite can be evaluated by the magnitude of the isomer shift. Here, the ferrous (Fe$^{2+}$) ions have positive isomer shift than ferric (Fe$^{3+}$) ions owing to the lower $s$-electron density at the nucleus due to greater screening of the $d$-electrons.

The excited state ($\frac{3}{2}$) of$^{57}$Fe nuclei splits into two substates $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$, thus forming a doublet owing to the interaction of nuclear quadrupole moment with the electric field gradient. The magnitude of the energy level splitting, called the quadrupole splitting ($\Delta$), is related to the nuclear quadrupole moment ($Q$) and the electric field gradient ($V_{ZZ}$) by the relation:

$$\Delta = \frac{eQV_{ZZ}}{2}$$ (2.18)

For the magnetic environment, as in the case of ferrites, the nuclear spin moment experiences a dipolar interaction in the presence of magnetic field, which causes the splitting of nuclear levels with a spin $I$ into $(2I+1)$ states or sextets, called hyperfine or Zeeman splitting. The line positions and corresponding spacing are proportional to effective magnetic hyperfine field ($B_{hf}$), while the line intensities are related to the angle between $\gamma$-ray and the nuclear spin moment. For the polycrystalline sample with no applied field, all lines are assumed to be Lorentzian with the ratio of area for six lines are 3:2:1:1:2:3. Thus, the Zeeman splitting of the spectrum gives a measure of the magnetic moment on the iron ions, while, the orientation of the magnetic moments are determined by the line intensities. In the simplest case, these interactions provide valuable information on chemical analysis together with the magnetic properties of the ferrites under investigation. For more extensive information on the theory and instrumentation, we have referred to collection of useful books$^{74-75}$ and website$^{76}$.

2.9.1.3 Raman Spectroscopy

Analogous to Mössbauer spectroscopy, Raman spectroscopy is another exception with a technique named (unabbreviated) after its inventor Prof. C. V. Raman. This technique in the most similar manner with XRD offers a unique fingerprint of the material under in-
vestigation and used to probe the molecular structure of crystalline material. It relies on inelastic scattering of monochromatic light which interacts with phonon, resulting in the energy of the Raman scattered radiation shifted from the incident radiation, which is called a Raman shift. In most studies of polycrystalline ferrites by Raman spectroscopy, the transitions observed in the atoms/lattices are vibrational and are covered in this subsection. Unlike other vibrational techniques like FTIR, Raman spectroscopy offers easy sample preparation. The technique is also versatile in terms of speed and ease in the characterization.

In a typical micro-Raman experiment, the ferrite is irradiated with monochromatic radiation (suitable laser light) and the inelastically scattered light is collected. Graphically, it plots the intensity of the scattered light as a function of Raman shift in wavenumber. The spectrum thus consists of number of symmetry-allowed peaks, called Raman active modes, and corresponds to one or more vibrational modes of the solids. However, the total number of peaks are less than or equal to number of Raman active modes, either due to degeneracy of few modes or the intensity of the few modes are too low to be measured. In the investigations of solids, the Raman activity is a function of space group symmetry of crystalline solids and the corresponding lattice vibrations provides information on strength of inter-atomic and intermolecular bonds, chemical composition/environment, degree of crystallinity and the mechanical strains present in a solid. The analysis of the Raman spectra demands the group theoretical analysis, which I referred from a classic textbook by F. Albert Cotton\textsuperscript{77}, while the useful text on Raman spectroscopy can be found in Characterization of Materials by E. N. Kaufmann\textsuperscript{78} and several other textbooks.

2.9.1.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope uses a focused beam of high energy electrons to generate a variety of signals at the surface of ferrites. The interaction of electron with ferrites or any other sample reveals information about the sample including morphology, chemical composition, and the crystalline structure. The advanced electron microscopes such as field emission SEMs (FE-SEM) probes the material under inspection at high magnification up to $\times800,000$ and has secondary electron image resolution of ca. 1 nm at 15 kV and 2 nm at accelerating voltage as low as 1 kV. The principle im-
ages produced in the SEM are secondary electron images and backscattered electron images, which are produced by different mechanism. By convention, when the energy of the emitted electron is less than about 50 eV, it is referred as secondary electron (SE). While, backscattered electrons (BSE) are referred to electrons that exit the specimen with energy greater than 50 eV. For BSE images, there is a built in contrast caused by elemental differences. These images provide information relating to morphological aspects of powder and topographical features of pellets and thick-film prints that employed in this work. Further, elemental mapping or spot chemical analysis can be performed by using energy dispersive X-ray spectroscopy (EDS). The basics of electron microscopy can be found in numerous textbooks and web sources including Refs. 78.

2.9.2 Magnetic Characterization: Vibrating Sample Magnetometer

Ferrites, a ferrimagnetic oxide materials exhibits spontaneous magnetization in the absence of external magnetic field. It results from the spontaneous ordering of atomic magnetic moments due to the exchange interaction among the electron spin. Thus, for a given ferrite material, the most important properties to be measured are its intrinsic magnetic properties viz. saturation magnetization and coercivity. They can be evaluated by measuring the magnetic moment (bulk) of the specimen as a function of external magnetic field on SQUID or VSM instrumentation. The magnetic characterization performed in the thesis only utilizes VSM for the measurement of magnetization ($\sigma_s$, $\sigma_r$) and coercivity ($H_c$). More details on the instrumentation and principle can be found in several texts, however, we have referred to a classic textbook of Physics of Magnetism and Magnetic Materials for the basics of VSM.

2.9.3 Electrical Characterization

The electrical and electronic measurements reveal the behaviour of a material in the given application. It also evaluates the characteristic of electronic component. The composition and chemical variations in the materials gives different electrical characteristic responses and useful in research and development of the targeted materials. These measurement are particularly relies on measurement techniques and test standard together with precise instrumentation, suitable test fixture and software. This Subsection
begins by describing measurement methods and their test fixture and test conditions, as applicable.

2.9.3.1 DC resistivity measurement

Resistivity is important of magnetic/ ferrite material because it contributes to penetration of microwave energy through it and it is this property which render ferrites invaluable for microwave applications over ferromagnetic metals (resistivity ~ $10^{-5}$ $\Omega$-cm). The measurement of resistivity is therefore important in understanding the pertinence of a material to microwaves.

Volume resistivity is a measure of leakage current directly through a material. The test sample is placed between two electrodes and a known potential is applied between them. The resulting current is measured using Keithley electrometer 6517A in combination with custom made resistivity jig. A custom made electrode configuration has been fabricated, depending on the size and shape of the specimen, which is discussed in detail in Keithley Application note series$^{80}$. The electrode dimensions and the volume resistivity measurement technique are shown in Figure2.12 (a) and (b).

**Fig. 2.12:** Volume resistivity measurement technique (a) Electrical set-up, (b) Circular electrode dimension$^{80}$

As preferred, the alternative polarity test at ±40 and ±100 volts for 60 seconds was performed for each measurement to eliminate the background currents. The resistivity is calculated from the geometry of the electrodes and the thickness of the sample:

$$
\rho = \frac{K_{\mu}}{t} \cdot \frac{V}{I}
$$

(2.19)
where: \( \rho \) = volume resistivity (\( \Omega \)-cm)

\( K_v \) = the effective area of the guarded electrode (cm\(^2\)) i.e.

\[
K_v = \pi \left( \frac{D_1}{2} \right)^2
\]  

(2.20)

\( V \) = applied voltage (volts)

\( I \) = measured current (amperes)

\( t \) = sample thickness (cm)

The resistivity may be used to determine/understand the phenomena relating to the dielectric breakdown, dissipation factor, mechanical continuity etc. of a material.

2.9.3.2 Permeability measurement

The permeability of a magnetic core is the characteristic that gives the core the ability to concentrate lines of magnetic flux. The application of an alternating-current magnetic field to a magnetic material will cause some magnetic loss and delayed induction of magnetic flux. Thus, permeability describes the interaction of a material with a magnetic field. The core material, as well as the core geometry, affects the core's “effective permeability”. For a given core shape, size and material and a given winding, higher permeability magnetic materials result in higher inductance values as opposed to lower permeability materials. Thus, high permeability allows higher inductance density, which is utterly required in modern magnetic components. High permeability materials are required to fabricate inductors.

Permeability in the alternating-current magnetic field is defined as complex relative permeability (\( \mu^*_r \)). The \( \mu^*_r \) can be expressed in vector diagram as shown in Figure 2.13.

**Fig. 2.13:** Vector diagram of complex relative permeability and loss tangent\(^{81}\)
where:
\[
\mu_r^* = \mu_r' - \mu_r'' \tag{2.21}
\]

\[
tan\delta = \frac{\mu_r''}{\mu_r} \tag{2.22}
\]

At high frequencies, the permeability separates into two components as shown in the vector diagram. The real component of the complex relative permeability (\(\mu_r'\)) represents the permeability with the magnetization in phase with the alternating-current magnetic field i.e. amount of energy stored in the magnetic material from the alternating-current magnetic field. While, the imaginary component (\(\mu_r''\)) indicates the magnetization that is out of phase with the alternating-current magnetic field. On the other hand, the ratio of imaginary component (\(\mu_r''\)) representing the losses in the material to the real component (\(\mu_r'\)) is expressed as magnetic loss tangent (\(tan\delta\)) as given by the Equation 2.22. The two permeabilities are often plotted on the same graph as a function of frequency, as in the case in this thesis, which is known as permeability dispersion or permeability spectrum. If we normalize the loss tangent per unit permeability, the material property which describes the loss characteristics per unit permeability is known as loss factor of a magnetic material.

To measure the relative permeability of the synthesized material, Agilent E4991A impedance/ materials analyzer was used in this work in combination with 16454A test fixture. The measurement technique uses the inductance method, in which the toroidal core is coiled with a wire to form a single-turn inductor and the \(\mu_r^*\) is calculated from the inductance value\(^{81}\). The measurement principle when using 16454A text fixture is shown in Figure 2.14.

![Measurement principles when using 16454A test fixture](image)

**Fig. 2.14:** Measurement principles when using 16454A test fixture\(^{81}\)
As shown in Fig. the self-inductance of a DUT is derived from the measurement of B induced by the current loop, I, which is given by

\[ L = \frac{1}{i} \int B \, ds \]  

(2.23)

\[
\begin{align*}
\int_{\frac{c}{2}}^{e} \int_{0}^{h_{0}} \frac{\mu_{0}}{2\pi r} \, dr \, dz + \int_{\frac{b}{2}}^{c} \int_{0}^{h_{0}} \frac{\mu_{0} \mu_{r}}{2\pi r} \, dr \, dz + \int_{\frac{c}{2}}^{h_{0}} \int_{\frac{a}{2}}^{h_{0}} \frac{\mu_{0}}{2\pi r} \, dr \, dz + \int_{\frac{b}{2}}^{h_{0}} \int_{\frac{a}{2}}^{b} \frac{\mu_{0}}{2\pi r} \, dr \, dz
\end{align*}
\]

(2.24)

where: \( \mu_{0} = 4\pi \times 10^{-7} \text{ H.m}^{-1} \) and \( \mu_{r} \) is relative permeability of the material.

\[ L = \frac{\mu_{0}}{2\pi} \left( (\mu_{r} - 1) h_{0} \ln \frac{c}{b} + h_{0} \ln \frac{e}{a} \right) \]  

(2.25)

By solving the above equation, the relative permeability of DUT is given by

\[ \mu_{r} = \frac{2\pi (L - L_{ss})}{\mu_{0} h_{0} \ln \frac{e}{a}} + 1 \]  

(2.26)

where, \( L_{ss} = \frac{\mu_{0}}{2\pi} h_{0} \ln \frac{e}{a} \) is the self-inductance of the test fixture without DUT. The measurement of \( L_{ss} \) is a part of short compensation (calibration process) to correct residual impedance due to the test fixture. As alternating current causes the inductance loss, the self-inductance \( L \) is expressed as a function of complex impedance as shown in Figure 2.15.
The self-impedance of the measurement circuit expressed as complex impedance is:

\[ L = \frac{Z^*}{j\omega} \]  

(2.27)

Substituting ‘L’ in Eq. 2.27 into Eq. 2.26, the complex relative permeability of DUT is expressed as

\[ \mu_r^* = \frac{2\pi(Z^* - j\omega k_{sc})}{j\omega \mu_0 \ln \frac{c}{b}} + 1 \]  

(2.28)

Given the measured impedance with DUT and no DUT mounted in the test fixture, i.e. \( Z_m^*Z_{sm}^* \) respectively, as shown in Figure 2.12, the complex permeability of DUT is expressed as

\[ \mu_r^* = \frac{2\pi(Z_m^* - Z_{sm}^*)}{j\omega \mu_0 \ln \frac{c}{b}} + 1 \]  

(2.29)

Equation 2.29, thus, gives the complex permeability of the device under test.

2.9.4 Measurement conditions For Characterization

A. X-ray diffraction (XRD)

Phase identification of the powder was performed by comparing X-ray powder diffraction data obtained with a Bruker D8 Advance X-ray diffractometer (Cu-K\( \alpha \) radiation: \( \lambda = 1.5418 \) Å) against the JCPDS standard database.

B. Electron microscopy

The morphological features (shape, size etc.) of the powders were examined by field emission scanning electron microscopy (FE-SEM: Hitachi S4800) at variable accelerating voltage and magnification. The microstructure of the sintered ferrite was examined by scanning electron microscopy (Philips XL 30) at accelerating voltage and magnification. The secondary electron imaging was performed for both cases. In few cases, back-scattered imaging was also performed to obtain better phase-contrast of multi-element system, such as LTCC stack containing LTCC, ferrite and conductor material.
C. **Raman spectroscopy**

Raman-scattering experiments in this work were performed in air at room temperature within 100 – 900 cm$^{-1}$. For BaFe$_{12}$O$_{19}$ polycrystalline hexaferrite powder, the equipment was JobinYvon Horiba LabRAM HR800 micro-Raman spectrometer. The spectra were excited with 632.8 nm radiation from air-cooled He-Ne laser. While, Raman-scattering experiments on NiCoZn spinel ferrite was performed on JobinYvon Horiba Lab-spectra HR800 micro-Raman spectrometer. The spectra were excited with 514.5 nm radiation from air-cooled Argon ion laser. Both spectrometers consisting a single spectrograph containing 1800 lines/mm grating, an Olympus microscope and a Peltier-cooled CCD detector. In all experiments, the laser power operated on samples were 10 mW or lower radiation by a suitable magnification lens to give a spot size of ca. 1 μm. All Raman-scattering experiments were non-polarized measurements with acquisition time ranged from 30 s to 3 min. The resolution in both cases was better than 2 cm$^{-1}$.

D. **Mössbauer spectroscopy**

In order to study the local lattice coordination and symmetry of the iron ions, Mössbauer spectra of powder samples was measured at room temperature. In Mössbauer spectroscopy (Nucleonix Systems Pvt. Ltd., India), the source employed was $^{57}$Co in Rh matrix of strength 50 mCi. The spectrometer was calibrated with $\alpha$-Fe metal foil and operated in a constant acceleration mode in transmission geometry. The Mössbauer spectra were fitted by using the WinNormos fitting program. The outer line width of calibration spectra was 0.29 mm/s.

E. **Magnetometry**

The magnetic properties such as saturation magnetization, coercivity, remanent magnetization were measured at room temperature by using a vibrating sample magnetometer. In case of M and Z-hexaferrites, the magnetic measurements were performed up to 17 kOe with ADE/DMS model EV7 magnetometer. In case of NiCoZn ferrite, the measurements were performed up to 10 kOe with Princeton Applied Research (PAR155) magnetometer.

F. **Sintered density**

The density of the sintered discs was evaluated by using Archimedes’s method.
G. **Bulk Resistivity**

The bulk resistivity was measured by performing alternating polarity tests on sintered discs mounted on a custom made test fixture (with ring and guarded electrode) in combination with Keithley 6517A high impedance electrometer. The electrodes of the custom made test fixture were built by following ASTM D-257 standard.

H. **Magnetic permeability measurements**

The frequency dependent magnetic properties were measured at room temperature in frequency range from 1 MHz to 1 GHz using Agilent E4991A Impedance analyzer equipped with 16454A magnetic material measurement test fixture. In this method, a toroidal core is coiled with a wire to form a single-turn inductor and the complex relative permeability, $\mu^*$ is calculated from the inductance values. The magnetic loss tangent, $\tan \delta (\mu)$ was calculated from the ratio of $\mu''$ and $\mu'$. All measurements were performed on non-oriented samples.

I. **Thermal expansion analysis**

The thermal expansion of the glass was measured using Dynamic Mechanical Analyzer (DMA: Perklin Elmer DMA 7e) in thermo mechanical analyzer mode (TMA), in the up to temperature 400 °C with heating rate 10 °C/min. The mean coefficient of the linear expansion value for the glass was calculated for the temperature range 150 to 250 °C.

J. **Optical microscopy**

Optical images and measurements were performed on Stereo microscope, Olympus SZX12 equipped with photographic attachment DP12.

K. **Thickness and warpage measurements**

Thickness and warpage measurement were performed using laser triangulation gauge on Talysurf CLI 2000 profilometer. The vertical resolution of the laser gauge was 1 µm.

2.10 **Conclusions**

The use of passive integration in LTCC meets the requirements of faster, smaller and better circuits for future electronics. In this Chapter, we have concisely reviewed the recent developments in the integration of magnetic passive components such as inductors,
filters, transformers etc. in low temperature cofired ceramic (LTCC) technology. The presently available integrated inductors in LTCC dielectrics are fabricated with very low inductance values. The inductance values can be increased, however, imposing constraints on self resonating frequency and dimensional scale of the component. Further, the integrated non-reciprocal devices are missing from already available rich variety of LTCC applications. This can be achieved by integrating ferrite with LTCC dielectric ceramics. However, the presently available materials are only limited to power electronic applications. Thus, in the given scenario, a search of new materials with improved magnetic properties will allow LTCC ferrite to be useful for high frequency signal electronic applications. One niche that is allowing LTCC ferrites to be useful for signal electronic applications is the search of new materials with improved properties. A thorough literature survey points towards NiCoZn ferrite and Z-type hexaferrite for VHF and UHF range inductors, respectively. On the other hand, M-type barium hexaferrite may useful for implementing integrated non-reciprocal devices in LTCC owing to its intrinsic anisotropy property required for intended applications. The chosen ferrites can be made available as LTCC ferrite materials only if they could be densified at temperature around 900 °C.

The chosen ferrites can be prepared by both conventional as well as combustion technique. Solid oxide method has been proven preparative conditions for spinel ferrites chosen for the work. On the other hand, combustion synthesis has been preferred for chosen hexaferrites, which allows formation of ferrites below 1200 °C. This method is also employed for the preparation of spinel ferrite in the thesis. Both synthetic methods are chosen based on the requirements of the grain growth and subsequent densification criteria of the sintered ferrites for improved performance properties. Grain growth during sintering can be better controlled if the initial size is small and uniform. This way porous-free sintered ferrites can be realized for high performance applications. Simultaneously, the literature review points towards the use of low temperature sintering additives/glass to bring down the densification temperature of ferrites close to 900 °C. This way the final sintered ferrites may be realized for their potential use in LTCC for integrated applications.

The next four Chapters focus on the developments of chosen ferrites and their compatibility study with LTCC.
References


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