Chapter 6

Compatibility Study of the Ferrites with LTCC

As seen in Chapter 1 and 2, the integration of magnetic components into existing LTCC dielectric would have a dramatic impact on the performance and miniaturization of the devices for applications in high frequency electronics. For such integration, the ferrite material must be co-fired with LTCC dielectric tape. Such LTCC compatible ferrite materials have applications integrated inductors, transformers, filters and non-reciprocal devices at RF and microwave frequencies. Fabrication of integrated magnetic devices in LTCC using ferrite can be accomplished in two different ways:

- **Fabrication and integration of ferrite tapes:** This approach utilizes magnetic materials formed into sheets / tapes having ferrite as main component. Individual tapes are processed together with standard LTCC fabrication as discussed in Section 2.1.1. These tapes are stacked and laminated together with LTCC dielectric tape or they can be used as standalone system. Finally, the cofiring is usually done below 900 °C to form the multilayer magnetic components. The technique can be used to fabricate integrated as well as multilayer magnetic components.

- **Ferrite thick-film paste:** A second approach to fabricate integrated magnetic components is the thick-film process in which individual ferrite compositions in paste form are sequentially deposited on LTCC substrates and finally, co-
fired. This technique can be used to fabricate integrated planar magnetic components.

Each of the techniques is necessary to implement integrated magnetic components. Since the aim of this work is limited to materials development compatible with LTCC host, we have chosen paste preparation of the ferrites developed here and studied the materials compatibility with commercial LTCC tapes.

Thus, this Chapter deals with the preparation of the thick-film ferrite paste, fabrication of test patterns on commercial LTCC tapes and studies of its materials and shrinkage compatibility with LTCC dielectrics and Ag based conductors. The thick-film processes as well as the common issues in co-sintering of the ferrite paste with LTCC are discussed.

6.1 Thick-film Process Technology

The generic term 'Thick films' is used for a processing methodology in which pastes are applied in a definitive pattern by screen printing, usually on an insulating substrate, dried, and subsequently fired. The function of these pastes, after firing in the solid state, is primarily determined by the characteristics of the functional material. The thick-film technology is has numerous applications in hybrid microcircuits. Conductors generally constitute largest quantity of thick film materials used in this technology. The other materials such as resistor and capacitor-dielectrics also found application in Hybrid Micro Circuits (HMCs), which are prepared on fired ceramic substrates. Similarly for LTCC, the paste of the desired functional material is screen-printed onto the green sheet by squeezing it over the screens with predefined pattern. In this method, the stress is applied to the paste by a squeegee, which applies shear force to the paste. The viscosity of the 'thixotropic' paste reduces under this force, and the paste flows through the openings of the screen. The paste regains its high viscosity after removal of shear force, allowing the printed patterns to retain the printed shape on the substrate. The thick-film process is illustrated in Figure 6.1.
One of the key factors in obtaining good quality circuit or passive device using thick film technology is good printing. In turn, good print quality is depends upon various factors, such as, screen specifications, printing process conditions, paste characteristics and green sheet characteristics. Among these, the printing process conditions and paste characteristics have the greatest impact on the print quality, assuming screen with optimum specifications and good quality and optimum green sheet characteristics. The screen specifications depend on the optimization of the mesh wire diameter together with the mesh count (defined as number of openings per sq. inch) and the thickness and quality of the emulsion. The green sheet with little surface roughness would be better for good quality print. On the other hand, print quality depends upon the squeegee speed, squeegee pressure, squeegee angle and snap-off (defined as the distance between the screen and the green sheet during printing). Since the present work does not cover optimization of the thick films and its printing, these issues are
not discussed in details here. Instead, the issues pertaining to the paste characteristics and paste formulation are discussed in brief, studied to and extent of obtaining working think film paste for materials characterization.

**Paste formulation and paste characteristics:**
A thick film paste is composed from three main constituents, namely, a functional material, permanent binder and a organic vehicle, sometimes called as temporary binder. The common materials used in thick-film paste are given in Table 6.1 along with the materials used in this study.

**Table 6.1:** Constituents used in thick-film paste and the materials used in this study

<table>
<thead>
<tr>
<th>Thick-film constituents</th>
<th>Commonly used materials</th>
<th>Materials used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional materials</td>
<td>Conductive, resistive, dielectric, magnetic</td>
<td>Inductive (ferrite materials)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1. NiCoZn spinel ferrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. BaFe$<em>{12}$O$</em>{19}$ hexaferrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Ba$<em>3$(CoZn)$<em>2$Fe$</em>{24}$O$</em>{41}$ hexaferrite</td>
</tr>
<tr>
<td>Permanent binder</td>
<td>Bi$_2$O$_3$, Cu$_2$O, PbO-WO$_3$, PbO$_2$, or low melting glasses such as lead-borosilicate, lead bismuth silicate, BBSZ glass etc.</td>
<td>Bi$_2$O$_3$ and BBSZ glass</td>
</tr>
<tr>
<td>Vehicle (organic) 1. Volatile phase 2. Non-volatile phase</td>
<td>Solvents: Terpineol, texanol etc. Binder and thixotropic materials: Ethyl cellulose, acrylates etc.</td>
<td>Texanol Ethyl cellulose,</td>
</tr>
</tbody>
</table>

The thick-film constituents and their functions are discussed below in brief.

**A. Functional material:**
The characteristic function of the paste depends upon the functional material, which is one of the inorganic materials contained in the paste. The materials can be conductive, resistive, dielectric or magnetic. The physical characteristics of the inorganic constituents including the functional material do have an influence on the print quality. These characteristics include particle size and shape, surface area distribution and the state of agglomeration of the function-
al material. In order to achieve good print quality, it is desirable to have narrow distribution of particles, centering around 1µm or below. It is also necessary to consider the particle size and surface area of the particles from the viewpoint of sinterability for dielectric and magnetic material or coalescence in case of conducting pastes. Submicron or finer sized particle distribution promote rapid densification and can be an effective means of lowering the sintering temperature. However, the finer particles tend to form agglomerates, which deteriorate the paste quality.

B. **Permanent binder:**

The function of the binder in the thick film paste is to promote adhesion of the functional material to the substrate without interfering with the intended function. Glasses are commonly used for as permanent binders. Adhesion to the substrate is achieved by a combination of mechanical and chemical means. The glass penetrates the capillaries between the ceramic particles and fluidizes readily. It wets the substrate, creating a mechanical bond to the substrate during firing. The glass also serves to accelerate the sintering of the inorganic material. If functional material's powder is having finer particle size and larger surface area, it is necessary to increase the amount of binder for shaping with the result that the filling ratio of the powder in the compact is low. Thus, during co-firing, the functional material sinters by means of a combination of solid state diffusion and reactive liquid phase sintering. Near peak firing temperature, particles of inorganic material can disperse / homogenize in the liquid glass phase to form glass-ceramic matrix and rapidly transport themselves. This accelerates the sintering process, allowing full densification which is to be achieved.

C. **Organic vehicle:**

The organic vehicle serves the functions of dispersing the thick film inorganic phases and making them screen-printable. The dispensability of the inorganic phases and the rheological characteristics of the thick-film paste are determined by chemistry and morphology of the dispersed phase and by the nature of the organic vehicle. The properties required in the dispersed phase are, to an
extent, determined by the performance needs of the fired films. Therefore, the vehicle becomes an important variable in developing suitable printing and functional behaviour. Viscosity is the most widely used parameter for assessing the rheological behaviour. The rheology is determined by the internal resistance exerted by a liquid to the relative motion of its parts, and is defined as shear stress divided by shear rate. Figure 6.2 illustrates four ways in which fluid can respond to shear stress. The viscosity of a Newtonian fluid is independent of shear rate, whereas a dilatant material becomes more viscous as the shear rate increases. Neither of these properties are suitable for screen-printing. Most of the conventional screen-printing materials exhibit pseudoplastic or thixotropic behaviour. The viscosity of these pastes decreases upon shearing and recover to high viscosity upon removal of the shear stress. A thixotropic material shows a degree of hysteresis, allowing leveling of mesh marks during the interval immediately after printing. Most thick film materials are formulated to give a specific level of thixotropy.

**Fig 6.2:** The viscous behavior of various kinds of fluids.
In addition to these three main constituents, dispersing agent and rheological additives may be added in small quantities to adjust viscosity, printability and shelf life.

6.2 Common issues involved in compatibility of ferrite material with LTCC

For a realistic integration of ferrites with LTCC, the ferrite material in the form of tape or paste must be co-fired with LTCC dielectric and metallization. Thus, compatibility becomes an important parameter. The key criteria for the compatibility of dissimilar materials are discussed below.

A. Sintering temperature:
The sintering temperature decides the densification behaviour of ferrite as well as LTCC material. The densification provides mechanical strength to the composite body by elimination of the porosity. This porosity in the sintered body is undesirable as it directly affects the mechanical, magnetic and electrical properties of the LTCC-ferrite composite structure. Therefore, in order to obtain porosity-free sintered body, it is necessary that the materials in the composite structure must be co-sintered (i.e. co-fired) at same temperature. For LTCC, the densification temperature is below 900 °C, which should be matched by ferrites. Therefore, in order to integrate ferrites with LTCC, there is a need to obtain full sintering in the ferrite material at or below 900 °C.

B. Chemical Inertness:
The undesired phases or a change in the local stoichiometry of the composite structure may affect the mechanical, electrical or magnetic properties. Therefore, chemical inertness between dissimilar material systems is necessary during co-firing as it avoids unwanted phase formation. In a similar manner, inter diffusion across the interface must be avoided since it also alters the local distribution of ions. Diffusion, however, cannot be avoided when joining dissimilar materials due to the chemical potential gradient across the interface. Inter diffusion, therefore, must be minimized or tolerated to some extent since the thermodynamic driving force for diffusion cannot be removed².


C. **Thermal Expansion:**
When dissimilar materials are joined (e.g. LTCC dielectric / conductor with ferrite tape / paste system) and subsequently co-fired, the temperature cycling or non-uniform heating of the substrate may lead to the differential expansion of the materials if the temperature coefficient of thermal expansion (CTE) are not matched. This introduces stresses and strains in the materials and joints leading to fracture in one of the materials, reducing life and reliability. Therefore, there is a need to accommodate the differential expansion of any of the material linearly with other materials.

D. **Shrinkage:**
The shrinkage matching is another criterion that must be satisfied to ensure the best possible mechanical properties of the multilayer composite structure. The dimensional shrinkage occurring in the multilayer co-fired ceramic systems is because of burning of polymeric binders used in fabrication of the green tapes, during firing. Shrinkage also depends on inorganic materials and process parameters to some extent. If the dimensional shrinkage of the different close-packed materials is different, it results in warping or fracture of the sintered parts. Therefore, there is a need to accommodate the shrinkage of the ferrite with LTCC tape system. In LTCC, for example, the dimensional shrinkage in the X and Y- direction is 12.7 ± 0.3%, while, shrinkage in Z-direction is 15 ± 0.5% for the DuPont 951 LTCC dielectric tape system. There is a need that the ferrite materials should match this shrinkage.

6.3 **Requirements of Glass-aided Sintering of Ferrites With LTCC**

The sintering of the ferrite is usually assisted by a small amount of additives, including low melting glasses. Typical additives for low temperature sintered ferrites are V$_2$O$_5$ $^{4,5}$, PbO $^{6,7}$, WO$_3$ $^8$, Co$_2$O$_3$ $^9$ and Bi$_2$O$_3$ $^{10-13}$. The main problem with these additives is the high porosity obtained in the sintered polycrystalline ferrites. The porosity can be reduced by high content of these non-magnetic phases (> 10 vol %), which, however, leads to reduced permeability. The deterioration of the magnetic properties is undesirable in many applications. Accordingly, the addition of low melting glasses, such as, Bi$_2$O$_3$–B$_2$O$_3$–SiO$_2$–ZnO (BBSZ) $^{14}$, CaO–B$_2$O$_3$–SiO$_2$ $^{15}$, lithium borosilicate glass $^{16}$, B$_2$O$_3$–Sb$_2$O$_3$ $^{17}$ or Al$_2$O$_3$–SiO$_2$–B$_2$O$_3$ $^{18}$ have also been reported. With these systems, the densification of the ferrite can be obtained below 900 °C. Another advan-
tage of using low melting glasses in LTCC is the expansion and shrinkage of the ferrite paste can be adjusted with LTCC by varying the glass content. Mismatch in the shrinkage for the Bi$_2$O$_3$-aided sintering of the ferrite was observed in this work, which is discussed in the Experimental section of this Chapter.

The typical glass systems added to ferrites are borosilicate, lead borosilicate or earth alkali glasses as listed above. However, due to a high content of non-magnetic phases, the permeability is dramatically reduced. Further, the use of lead (Pb) in the system has restriction due to environmental concern. A novel technique to solve this problem and to achieve the densification below 900 °C is the use of reactive glasses such as BBSZ glass. The use of BBSZ glass for LTCC system is widely explored$^{19-24}$. Further, it is known that the glass system is inert to LTCC compositions as well as ferrite compositions.

6.4 Experimental

6.4.1 Preparation of BBSZ Glass
As seen above, BBSZ glass was chosen as additive to ferrite pastes for integration with LTCC host. The selection of the glass was purely based on the literature survey. The reactive sintering glass composition containing 27 mol% B$_2$O$_3$, 35 mol% Bi$_2$O$_3$, 6 mol% SiO$_2$ and 32 mol% ZnO glass (BBSZ glass) was prepared in the following way. All oxide powders were used as-received from Sigma-Aldrich Chemicals with purity upward of 99.99+ % except for Bi$_2$O$_3$, which had 99.9+% purity. The oxide powders were taken the stoichiometric amount and ball milled in the anhydrous solution of acetone and isopropyl alcohol to obtain homogenize mixture of the powders. Firing of the as-obtained mixture was done in platinum crucible at a temperature of 1000 °C for 1 h. and quenched in distilled water to obtain the glass frit. The as-formed BBSZ glass frit was again ball milled to obtain the micron sized particles. The glass powder was used with ferrite to prepare the paste.

6.4.2 Ferrite thick film paste preparation
To study the compatibility of the synthesized ferrite powders with LTCC, the thick-film paste of the synthesized ferrite viz. NiCoZn spinel ferrite (Chapter 3), BaFe$_{12}$O$_{19}$ hexaferrite (Chapter 4) and Ba$_3$(CoZn)$_2$Fe$_{24}$O$_{41}$ hexaferrite (Chapter 5) were prepared.
The samples chosen for this study and constituents used in the paste formulation are given in Table 6.2.

**Table 6.2:** Ferrite thick-film paste formulation conditions

<table>
<thead>
<tr>
<th>Ferrite material &amp; specifications</th>
<th>Paste code</th>
<th>Paste formulation</th>
<th>Paste formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferrite type</strong></td>
<td><strong>Sample name</strong></td>
<td><strong>Particle size (μm)</strong></td>
<td><strong>Functional material</strong></td>
</tr>
<tr>
<td>NiCoZn ferrite (Chapter 3)</td>
<td>DW8</td>
<td>0.5 - 1</td>
<td>Paste_1*</td>
</tr>
<tr>
<td></td>
<td>DNS8</td>
<td>&lt; 0.6</td>
<td>Paste_2</td>
</tr>
<tr>
<td></td>
<td>DAT2</td>
<td>&lt; 0.6</td>
<td>Paste_3</td>
</tr>
<tr>
<td>BaFe₁₂O₁₉ hexaferrite (Chapter 4)</td>
<td>B</td>
<td>2 - 5</td>
<td>Paste_4</td>
</tr>
<tr>
<td>Z-hexaferrite (Chapter 5)</td>
<td>1X3</td>
<td>2 - 5</td>
<td>Paste_5</td>
</tr>
</tbody>
</table>

* Bi₂O₃ was used only in Paste_1 as a permanent binder, which also functions as sintering aid. Based on the results obtained in this experiment, BBSZ glass powder was used in other paste.

** The weight percentage of function material was fixed to 98 %, whereas the permanent binder is 2 wt% in total 75 wt% of inorganic constituents

The corresponding ferrite paste was prepared thoroughly mixing sub-micron/ micron size particles of inorganic functional material with inorganic permanent binder Bi₂O₃ or BBSZ glass in a weight ratio of approximately 98:2 ratio. The Bi₂O₃ was used only in ‘Paste_1’, which also functions as sintering aid. Other ferrite pastes (‘Paste_2’ to ‘Paste_5’) were prepared using BBSZ glass powder including ‘Paste_1’. The Bi₂O₃ powder used in these experiments had purity upward of 99.9 % and particle size around 100 nm as per the manufacturer’s certification (Sigma-Aldrich; Batch # 07603AE). The BBSZ powder used here was has a particle size less than 3 μm (Fig. 6.6). The preparation conditions for the BBSZ glass powder are already discussed in Section 6.4.1. This inorganic mixture was then dispersed in an organic medium composed of the *ethyl cellulose* (CH₂CH₃; AR grade) in an organic solvent *texanol ester alcohol* (2,2,4-Trimethyl-1-3-pentanediol Monoisobutyrate; Sigma-Aldrich Chemicals), with an inorganic to organic weight ratio of approximately 75:25, as given in Table 6.2. Finally, the inorganic and organic part was thoroughly mixed to obtain a
homogeneous pasty blend. The thick-film paste was applied on the screen and the paste was transferred to DuPont 951 LTCC 4-layer green stack (LTCC layer thickness ~250μm each) and silver pattern through the screen-mesh with the help of squeegee. The thick-film paste was then sandwiched between LTCC stack in few samples of each paste to study the interface. In some samples, the ferrite layer was made on the top surface. These stacks were finally subjected to lamination at 70 °C for 10 min. in an isostatic laminator, followed by co-firing at 900 °C for 2 h. following standard LTCC firing cycle with change in dwell time at peak temperature\textsuperscript{25}. The 875-900 °C is recommended sintering temperature for the LTCC sintering. The firing profile used for this study is shown in Figure 6.3. The thick-film process is explained earlier in Section 6.1. The schematic of the ferrite thick film is shown in Figure 6.4.

**Fig. 6.3:** Firing profile for ferrite thick-films with LTCC

**Fig 6.4:** Cross-sectional schematic of ferrite thick film paste sandwiched between silver & LTCC
6.5 Results and Discussions

6.5.1 Characterization of BBSZ glass powder
The BBSZ glass powder prepared was characterized by X-ray diffraction and field emission scanning electron microscopy to identify the glassy nature and particle size distribution, respectively. Thermal expansion of the glass powder was studied to understand shrinkage behaviour. The results are presented below.

![XRD pattern of BBSZ glass](image)

**Fig. 6.5:** XRD pattern of BBSZ glass

Figure 6.5 presents the X-ray diffraction (XRD) pattern of the BBSZ glass powder. The XRD pattern shows absence of sharp narrow diffraction peaks corresponding to the crystallinity of the synthesized powder. Instead, a very broad peak (halo) was observed which is an indication of the amorphous nature of the powder. The field-emission SEM micrograph (10000×) of the BBSZ glass powder is presented in Figure 6.6.
It is observed from the micrographs that the particle size varies between 0.5-3µm. This particle size distribution is usually acceptable for the thick film pastes\(^1\). The thermal expansion of the BBSZ glass powder was measured by DMA/ TMA analyzer. Figure 6.7 shows the thermal expansion curve for the BBSZ glass.

The mean coefficient of the linear expansion value for the temperature range 150 to 250 °C was calculated and determined to be \(8 \times 10^{-6} \text{ (1/°C)}\) \(i.e.\) 8 ppm/°C. The value is close to the expansion coefficient of DuPont LTCC 951 Tape, which is 5.8
This expansion of the glass could be acceptable for its use of LTCC. The glass may have softened at about 355 °C, as seen from the Figure 6.7.

Thus, it is concluded that the as-synthesized BBSZ glass can be useful with LTCC environment.

### 6.5.2 Characterization of the ferrite pastes

#### A. Material Interaction

X-ray diffraction analysis of the co-fired ferrite paste pattern on LTCC and silver was compared to that of individual materials to identify new phases. The thick-film paste used in this analysis was sintered at 900 °C for 2 h., as discussed earlier. Figure 6.9 (a to c) shows XRD pattern for the fired ferrite thick film printed on LTCC substrate, whereas, Figure 6.10 (a to c) shows the XRD pattern for the fired ferrite thick film printed on silver conductor, which is printed on LTCC substrate. Figure 6.8 (a & b) shows the optical micrographs of the ferrite thick-film paste printed on LTCC and Ag electrode.

![Fig. 6.8: Optical micrographs of representative ferrite thick-film paste (sintered) on (a) LTCC substrate, and (b) on silver pad](image)
Fig. 6.9: XRD pattern of ferrite (sintered) thick-film paste printed on LTCC substrate for the samples (a) NiCoZn spinel ferrite ‘Paste_1 to 3’, (b) BaFe$_{12}$O$_{19}$ hexaferrite ‘Paste_4’, and (c) Z- hexaferrite ‘Paste_5’
It is observed from the Fig. 6.9 and 6.10 that the peaks correspond only to the diffraction peaks of constituent material. Therefore, it is concluded that there is no noticeable chemical interaction between ferrite and LTCC or silver. For the diffraction pattern shown in Fig. 6.10, it is seen that higher intensity peaks are observed at 38.30°, 44.27°, 64.35° and 77.40° are corresponds to silver (JCPDS card # 4-0783).

It is concluded that for the present materials compositions, the LTCC host, silver and ferrites are chemically inert to each other even after co-sintering, implying the suitability of the ferrite materials for LTCC applications. However, it may be necessary to study the interface between ferrite and LTCC/silver by SEM/EDS analysis at the interface. This may throw light on diffusion across the interface. The results pertaining to this study are discussed in the following sub-Section.

**B. Microstructural Study**

The microstructure of the sintered ferrite is important since the densified ferrite, free from porosity, is desirable to obtain the optimum magnetic properties at high frequency. Figure 6.11 (a to e) shows SEM micrographs of the co-sintered ferrite paste on/with LTCC.

**Fig. 6.10:** XRD pattern of ferrite (sintered) thick-film paste printed on silver conductor for the samples (a) NiCoZn spinel ferrite ‘Paste_1 to 3’, (b) BaFe_{12}O_{19} hexaferrite ‘Paste_4’
SEM analysis performed on the top surface of the ferrite pattern on LTCC shows porous microstructure of the sintered ferrite, which is generally undesirable. The absence of dense microstructure is mainly attributed to the inhomogeneous mixing of the glass and ferrite. This can be observed from the selected SEM micrographs show-

Fig. 6.11 (a to e): Top surface SEM micrographs of the ferrite paste co-sintered with LTCC for the Paste_1 to Paste_5, respectively.

SEM analysis performed on the top surface of the ferrite pattern on LTCC shows porous microstructure of the sintered ferrite, which is generally undesirable. The absence of dense microstructure is mainly attributed to the inhomogeneous mixing of the glass and ferrite. This can be observed from the selected SEM micrographs show-
ing glass-rich and glass-deficient regions in the microstructure. These results are shown in Figure 6.12 (a & b) for representative pastes (Paste_4 & 5). The glass-rich and glass-deficient regions are marked in the micrographs as ‘G-R’ and ‘G-D’, respectively. It is clearly seen that the glass-rich regions show relatively dense microstructure than the glass-deficient region. However, it is also likely that the sintering time for the interaction between glass and ferrite was insufficient in this region. Apart from the homogeneous mixing of the glass with ferrite, it must be necessary to increase the sintering duration to complete the physical interaction between these inorganic constituents. The increase in the sintering duration allow complete wetting of the ferrite surface by glassy matrix and the grain growth mechanism would take place between the ferrite grains, helping in improving the densification of the ferrite. However, it is seen that grain diffusion could not take place in most part of the ferrite. This condition is applicable to all ferrite paste investigated in this study. Another reason for the incomplete sintering is attributed to the optimization issue pertaining to the ratio of the organic to inorganic constituents. Based on these results, it is concluded that the ferrites have shown has poor microstructure which may improve with appropriate glass content and processing conditions.

![Fig. 6.12 (a & b): Top surface SEM micrographs of the ferrite paste co-sintered with LTCC for the Paste_4 to Paste_5, respectively (G-R: glass-rich and G-D: glass-deficient)](image)

C. Interface Study

The extent of the ferrite cation diffusion into LTCC or silver is important since any reaction at the interface between these dissimilar materials may affect the magnetic
Chapter 6

and electric properties of the final device. Figure 6.13 (a to e) shows cross-sectional SEM images of the LTCC-silver-ferrite interface.

![Cross-sectional back-scattered SEM micrographs of the ferrite paste co-sintered with LTCC and Ag for the Paste_1 to Paste_5, respectively.](image)

**Fig. 6.13 (a to e):** Cross-sectional back-scattered SEM micrographs of the ferrite paste co-sintered with LTCC and Ag for the Paste_1 to Paste_5, respectively.

SEM analysis performed on the interface of ferrite and LTCC/Ag show no change in the LTCC and ferrite microstructure at the interface. The silver diffusion into ferrite is seen from the back-scattered SEM images. The silver diffusion into ferrite film may
be attributed due to two reasons. First, the diffusion-like image seen in the Fig. 6.13 (d & e) with (*) marked region may be attributed to spreading of silver over the interface while cutting, due to malleable nature of the silver. It may be noted that the cross-section of the LTCC-ferrite structure is taken by cutting using high-speed diamond saw (10k rpm), and observed as-cut. Further, the fired film thickness of the ferrite layer is around 15 μm. Thus, there is a possibility of the silver particles on the surface of the ferrite film as seen in the star (*) marked region. Second possibility is of diffusion of the silver into around the poorly sintered ferrite particles. The porous nature of the film is seen in the film magnified above 1000× i.e. Fig. 6.13 (a, c, & d). Further, no de-lamination and cracks were observed between the ferrite-silver interface and ferrite-LTCC interface, thus confirming the sufficient bonding exist between sintered ferrite and LTCC/ silver layers. Furthermore, evenly distributed glass matrix is clearly seen in the back scatter SEM images of the LTCC layer. Unlike the LTCC layer, glass distribution is difficult to observe as the ferrite layer contains very small amount of BBSZ glass (2 wt%). Even with the lower glass content, shrinkage matching of the ferrite layer with LTCC and silver layer during cofiring is accomplished, which is discussed in next section.

D. Shrinkage and Surface Roughness

The shrinkage in the X-Y direction is another necessary aspect that must be satisfied to ensure the compatibility of the ferrite with LTCC. The shrinkage of the ferrite test pattern was found by measuring the ferrite pattern X-Y dimensions and warpage due the pattern. To measure the shrinkage, ferrite paste of the DW8 sample were initially prepared by adding 4 and 8 wt% Bi₂O₃ to the ferrite compositions. The samples names for 4 and 8 wt% Bi₂O₃ are referred as ‘Paste_1_Bi-4’ and ‘Paste_1_Bi-8’, respectively. The shrinkage data of the ferrite pattern is given in Table 6.3.

**Table 6.3:** X-Y shrinkage data of the ferrite paste with Bi₂O₃ as sintering additive

<table>
<thead>
<tr>
<th>Sample come</th>
<th>Test pattern</th>
<th>Unfired (in mm)</th>
<th>Fired (in mm)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>X</td>
<td>Y</td>
<td>X</td>
</tr>
<tr>
<td>Paste_1_Bi-4</td>
<td>Pattern_1</td>
<td>10.58</td>
<td>3.34</td>
<td>9.76</td>
</tr>
<tr>
<td>(DW8)</td>
<td></td>
<td>10.58</td>
<td>3.30</td>
<td>9.79</td>
</tr>
<tr>
<td>Paste_1_Bi-8</td>
<td>Pattern_1</td>
<td>10.60</td>
<td>3.49</td>
<td>9.80</td>
</tr>
<tr>
<td>(DW8)</td>
<td></td>
<td>10.50</td>
<td>3.39</td>
<td>9.70</td>
</tr>
</tbody>
</table>
The shrinkage measurement of the Bi$_2$O$_3$-aided sintering of the ferrite paste shows shrinkage in the range of 8-10\% in X-Y direction even with 8 wt\% content of Bi$_2$O$_3$ in ferrite paste. The shrinkage mismatch in the ferrite and LTCC layer resulted in bulging in the ferrite test-pattern region, which is unacceptable condition for the compatibility studies. Therefore, further experimentations on pastes were not carried with Bi$_2$O$_3$ sintering additive. Further, higher content of Bi$_2$O$_3$ may deteriorate the magnetic and electrical properties of the ferrite. It is reported that the presence of Bi$_2$O$_3$ in NiCuZn ferrite multilayer chip inductor (MLCI) has adverse effect due to reaction between silver electrodes during sintering$^{2,26}$.

Therefore, proper glass chemistry with appropriate sintering and shrinkage behaviour was selected for co-firable ferrite with LTCC. A survey on the relevant literature is already discussed in Section 6.3. It is seen that the BBSZ glass is suitable candidate as a sintering additive for ferrites, as well as shrinkage characteristics. The expansion of the BBSZ glass is also matching with that of LTCC. Therefore, the next sets of ferrite paste were prepared with the use of BBSZ glass as sintering aid and permanent binder in the paste formulation. The shrinkage data of these ferrite patterns is given in Table 6.4.

**Table 6.4:** X-Y shrinkage data of the ferrite paste with 2 wt\% BBSZ glass

<table>
<thead>
<tr>
<th>Sample come</th>
<th>Test pattern</th>
<th>Unfired (in mm)</th>
<th>Fired (in mm)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>X</td>
<td>Y</td>
<td>X</td>
</tr>
<tr>
<td>Paste_1 (DW8)</td>
<td>Pattern_1</td>
<td>6.81</td>
<td>6.16</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>7.05</td>
<td>2.91</td>
<td>6.21</td>
</tr>
<tr>
<td>Paste_2 (DNS8)</td>
<td>Pattern_1</td>
<td>14.38</td>
<td>14.53</td>
<td>12.61</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>2.52</td>
<td>2.49</td>
<td>2.20</td>
</tr>
<tr>
<td>Paste_3 (DAT2)</td>
<td>Pattern_1</td>
<td>7.02</td>
<td>3.06</td>
<td>6.30</td>
</tr>
<tr>
<td>Paste_4 (B)</td>
<td>Pattern_1</td>
<td>6.75</td>
<td>6.03</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>6.96</td>
<td>××××</td>
<td>6.25</td>
</tr>
<tr>
<td>Paste_5 (1X3)</td>
<td>Pattern_1</td>
<td>7.02</td>
<td>6.09</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>7.02</td>
<td>2.91</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>14.35</td>
<td>14.29</td>
<td>12.36</td>
</tr>
<tr>
<td></td>
<td>Pattern_2</td>
<td>2.34</td>
<td>2.34</td>
<td>2.10</td>
</tr>
</tbody>
</table>

×××× Measurements are not performed.
Shrinkage analysis of the ferrite paste showed shrinkage in the range of 11 to 15%
% in X-Y direction without any bulging. As discussed earlier, the dimensional shrin-
kage in the $X$ and $Y$- direction for the DuPont 951 LTCC dielectric tape system is $12.7$
$\pm 0.3\%$. The variation in the shrinkage is attributed to the inhomogeneous mixing of
the BBSZ glass with ferrite powder. It was concluded that the good shrinkage match-
ing is observed due to the use of glass content in the ferrite.

E. Surface Roughness and Film Thickness

Surface roughness and film thickness were measured by laser triangulation method
with accuracy of $1 \mu m$ using Tallysurf CLI 2000. The film thickness scan and surface
profile for selected region of the ferrites pastes is presented in Figure 6.14 and Figure
6.15, respectively.
Fig. 6.14 (a to e): Thickness profile scan of the ferrite paste on the LTCC substrate for the Paste_1 to Paste_5, respectively
The surface scan of the ferrite paste reveals the fired thickness of the ferrite for the ‘Pastes_1’ to ‘Paste_5’ were 18, 20, 22.5, 17.5, 23.2 μm, respectively. On the other hand, surface roughness for the ‘Pastes_2’ to ‘Paste_5’ was 3.6, 2.7, 4.5 and 4.2 μm, respectively. The warpage of the substrate was measured using single line scan of the whole substrate, which is shown in Figure 6.16 (a to e). A little bulge is seen on the sintered LTCC substrate when co-fired with ferrite layer. This warpage is attributed to the un-optimized firing conditions and paste composition of the ferrites, which has led to poor sintering. It can also be seen that the overall paste characteristic greatly influences the final substrate quality in terms of quality of the printed film, surface roughness, warpage, fired density of the sample etc. Although a comprehensive optimization of paste properties was not a part of this study, the present study confirms the compatibility of all synthesized ferrite layers with LTCC. More work is needed to optimize the synthesized ferrite material with LTCC, which is discussed in detail in Chapter 7.

Fig. 6.15 (a to d): Surface profile of the sintered ferrite paste on LTCC for the Paste_1 to Paste_5, respectively
6.6 Conclusions

The thick-film paste of NiCoZn ferrite (Paste_1 to 3), BaFe$_{12}$O$_{19}$ hexaferrite (Paste_4) and Ba$_3$Co$_x$Zn$_{2-x}$Fe$_{24}$O$_{41}$ hexaferrite (Paste_5) were prepared to investigated the compatibility of the synthesized material with commercially available LTCC dielectric.
tapes. Co-firing of all ferrite pastes was performed on DuPont LTCC dielectric tape. All co-fired samples resulted in defect-free LTCC substrate with integrated ferrite layer on top and middle of the LTCC substrate. Upon co-firing of the ferrite with LTCC dielectrics and silver, no new material phase was observed at the interface of these materials. The interfacial study reveals no diffusion from dielectric and silver layer into ferrite layer and vice versa. The silver diffusion in the ferrite layer, if any, to some extent is due to the porous nature of the film, which can be reduced by optimizing the densification behaviour of the ferrite layer with LTCC. The interface study also reveals adequate bonding of the ferrite layer with LTCC layer. No cracks, delamination was observed at the interface. Further, the porous microstructure was obtained in all ferrites when co-fired with LTCC. The porous microstructure, which is undesirable for high frequency applications, can be avoided with optimization of the paste properties, glass properties and preparation etc, finally optimizing the densification behaviour of ferrite layer with LTCC. The shrinkage behaviour of all ferrites paste was matched to that of commercial LTCC tape material upon co-firing. The BBSZ glass was used to accommodate the shrinkage of the ferrite paste with LTCC, which can also be used as sintering aid apart from permanent binder. An alternative approach of using high concentration of Bi$_2$O$_3$ (up to 8 wt %) cannot produce 13% shrinkage in X-Y direction to match with the LTCC shrinkage. The closely matching TCE of BBSZ glass with LTCC may have resulted in better physical properties of the fired substrate. Accordingly, the sandwiched as well as placed on the top layer ferrite thick-film pattern of LTCC does not show any de-lamination, cracks, unacceptable warpage in the fired substrate.

In essence, the preliminary results of ferrite integration with LTCC shows that the synthesized ferrite material possesses acceptable compatibility with the LTCC in paste form, indicating that the developed ferrite materials can be used to fabricate planar or 3D integrated magnetic devices in LTCC. However, extensive optimization of the pastes is necessary.
References


