Chapter 4

Development of $\text{BaFe}_{12}\text{O}_{19}$ Hexaferrite

This Thesis is concerned with the RF/ microwave ferrites for their use in LTCC. The frequencies of interest are above 100 MHz in RF domain to few tens of GHz in microwave ranges. In this frequency range, two types of ferrite based devices have been implemented, namely:

- The ferrites with suitable scalar permeability which can be used in RF frequency ranges, for instance to fabricate devices such as inductors, are considered as soft ferrites. The pertinent topic is dealt with in Chapter 3 and 5 of this Thesis. These ferrites are the non-microwave ferrites.

- Another type is microwave ferrites, which are again classified with two types of devices, namely ferrites for reciprocal and non-reciprocal devices. For reciprocal applications, such as, electrically controlled phase shifters, ferrites can be used. However, there are other high performance alternative materials or devices to fabricate these devices viz. ferroelectric materials and the devices that are based on semiconductor diodes. Therefore, ferrite materials for reciprocal applications are not the topic of interest in the thesis.

The other type of devices, i.e. the non-reciprocal devices, such as, circulators and isolators, find a large number of applications. Ferrites are necessary for the fabrication of these devices. Such ferrites are the topic of interest of this Chapter.
4.1 Generic Materials Selection Criteria vis-à-vis Their Properties for Fabrication of Non-reciprocal Devices

In the previous Chapters we have seen that spinel ferrites along with garnets have been used in many microwave applications ranging from 1 -10 GHz. Hexaferrite is another class of materials that has proven to be versatile for applications from 1 -100 GHz. The major advantage of using hexaferrites over spinel and garnets is that the materials do not require a permanent magnet when used for microwave frequencies. The elimination of the permanent magnet from the device saves space and cost of the device. This is one of the most sought after technical specification for such applications. The materials property which contributes to this advantage is the topic of discussion in this Section.

The Hexaferrites exhibit a c-axis symmetry and high magnetocrystalline anisotropy. In the absence of external bias field, the crystallites are oriented by the intrinsic magnetic field (due to magnetocrystalline anisotropy) in order to align it to the c-axis. This is called the self-biased property. Therefore, when the microwave field is applied in a plane perpendicular to the magnetization direction, a gyromagnetic resonance occurs. The resonance frequency, \( f_r \), is related to the applied field (in the direction of magnetization), but allowing for an anisotropy field \( H_a \), such that,

\[
f_r = \left(\gamma \mu_0 / 2\pi\right) \left\{ [H_z + H_a + (N_x - N_z)M_s][H_z + H_x + (N_y - N_z)M_z] \right\}^{1/2} \tag{4.1}
\]

where, \( f_r \) is the resonance field, \( N_x, N_y, \) and \( N_z \) are the demagnetization factor in the x, y and z-direction, \( H_a \) is the anisotropy field, \( \gamma \) is the gyromagnetic ratio.

Owing to the high values of \( H_a \) which may be up to 2780 kA/m (35 kOe), resonance may occur at millimeter wave frequencies in the absence of external bias field, \( H \), or with a weak field, \( H \), which is easy to handle\(^1\). Thus, when the ferrites are magnetized, they act in non-reciprocal manner, which means their characteristics depend on the direction of motion of the wave passing through them. This non-reciprocity is exploited to build critical devices employed in radar systems, mobile telephone relay stations, etc. Thus, anisotropy in the propagation of the electromagnetic (EM) wave gives rise to directional absorption or a non-reciprocal rotation of the plane of polarization of the EM wave, a non-reciprocal phase shift or a non-reciprocal displacement of the microwave field pattern. These different properties are used to build the devices like isolators,
circuitors etc. For example, when the field is along the c-axis and if the microwave signals are propagated perpendicular to c-axis, the electron spins rotate in the same direction as the RF magnetic field. On the other hand, when the propagation of the microwave signals reversed, the RF magnetic field will rotate in an opposite sense to the electron spins and no interaction occurs. These two cases correspond to the attenuation in one direction and little or no attenuation in opposite direction\(^2\). This way, the microwave isolators capitalize on the non-reciprocal properties of ferrites. The characteristics related to the use of hexaferrites at the microwave frequencies for non-reciprocal applications are\(^3\)-\(^7\):

- **Saturation magnetization** \((4\pi M_s)\):
  The role of magnetization is fundamental and is a factor in all the magnetic susceptibility, therefore determines the usefulness of material. The magnetization and susceptibility may be approximately represented by:

\[
\chi_+ = \frac{M_s}{H-H_r+j(\Delta H/2)} \quad \text{and} \quad \chi_- = \frac{M_s}{H+H_r+j(\Delta H/2)}
\]

(4.2)

where, \(\chi\) is the susceptibility term, \(H_r\) is the resonance field, \(\Delta H\) is the line width and \(M_s\) is the saturation magnetization.

Therefore, to obtain the highest possible susceptibility term, it would be necessary in all cases to choose the highest possible magnetization. The magnetization also "sets" the value of the internal dipolar fields in the natural resonance effect (in the demagnetized state), which is of prime importance in the choice of a material for a given application.

- **Permeability and effective line width**:
  The microwave applications make use of the permeability of the ferrite which is determined by phenomenon of resonance. The permeability depends on the magnetization and the applied static magnetic field, as well as on the frequency and polarization of the electromagnetic wave, with respect to the static field. When a circularly polarized wave propagating parallel to the static field, the permeability will depend on the sign of the polarization (forward or reverse direction of propagation), by the equation:

\[
\mu_\pm = 1 + \chi_\pm
\]

(4.3)
\[ \chi = \chi' - j\chi'' \quad (4.4) \]

where, \( \chi \) is the susceptibility as given from the Equation 4.2.

In case of saturated materials, the curves of \( \mu'_+ \) and \( \mu''_+ \) have a shape which is characteristic of a resonance. This property is shown in Figure 4.1, which is used in construction of non-reciprocal devices. The curve represents main features such as resonance field (\( H_r \)), line width (\( \Delta H \)), effective gyromagnetic factor (\( g_{\text{eff}} \)) and gyromagnetic resonance frequency, which are important terms in designing the non-reciprocal applications.

**Fig. 4.1:** Real and imaginary part of permeability of circular polarization (\( \mu'_+ \) and \( \mu_+ \)) versus static magnetic field \( H \). \( \mu'_+ \) and \( \mu''_+ \) are plotted at \( H > 0 \), \( \mu'_- \) is plotted at \( H < 0 \) and \( \mu''_- \) equal practically zero at any field.

Line width, \( \Delta H \) define the magnetic loss at gyromagnetic resonance (value at \( \mu''_{\text{max}}/2 \)), which sets the useful bandwidth of the device. Therefore, low \( \Delta H \) presents a high localization of magnetic losses around gyromagnetic resonance frequency.

- **Magnetocrystalline anisotropy:**
  Magnetocrystalline anisotropy refers to the dependence of the internal energy on the direction of magnetization. The source of this anisotropy is related to the preference of the direction of the magnetic moment to the certain crystallographic directions as a result of spin-orbit and orbit-lattice coupling. This property give rise to the high internal bias field, called *self-biased property* (up to 35 kG in case of hexaferrites),
which is used to eliminate the external bias field usually provided by the permanent magnets in microwave applications. The use of the permanent magnets results in bulky microwave devices. The intrinsic high anisotropy field is essential to design miniaturized non-reciprocal microwave applications. The logic behind using ferrite materials with high magnetocrystalline anisotropy is discussed earlier in this Section, whereas the selection of the materials based on anisotropy field will be discussed in next Section.

- **Coercivity:**
  The ferrites are classified as soft and hard ferrites. The basis of this division is coercivity, $H_c$, which is the mean critical field necessary to bring the induction to zero in the direction of the field. For microwave applications, the value of coercivity must be small to minimize the control power requirement. Coercivity is not only determined by the domain structure, but is also depends on the shape and magnetic anisotropy effects, grain boundaries, inhomogeneities, pores etc., which increases microwave losses to an unacceptable level. Therefore, low coercivity along with the demagnetizing energy shears the easy axes loop and results in the loss of self-biased properties. This reduces the need to increase coercivity and maintain low microwave loss.

- **Magnetic losses:**
  Loss from the ferrite materials are linked with magnetic and dielectric loss. The magnetic losses can be distinguished at low and high microwave power level. The magnetic losses will occur in the ferrite material up to a frequency limit corresponding to resonance field $H_r$, equal to or lower than $M_s$.

- **Dielectric losses:**
  The dielectric losses, $\varepsilon''$ (or the loss tangent, $\tan \delta = \varepsilon'' / \varepsilon'$) results from the existence of iron in two states of valence: trivalent and divalent. This results in an excess of electrons which may jump from one Fe ion to another and thus causes electronic conduction and consequently dielectric losses. This explains the necessity of ferrite composition free from divalent Fe ions. The dielectric loss angles of $10^{-4}$ at 10 GHz are required for these applications.
• **Resistivity:**

High resistivity is required to ensure the complete penetration of microwave frequencies. High resistivity ferrite minimizes the eddy current losses at these frequencies. As given above for the dielectric losses, the higher resistivity (must be above $10^9 \ \Omega \cdot \text{cm}$) can be obtained with the elimination of divalent Fe ions from the ferrite composition.

In conclusion, ferrites must possess high saturation magnetization, low coercivity, high remanent magnetization, reasonable magnetic anisotropy field, high ferromagnetic resonance, low resonance line widths, high resistivity, low magnetic losses and low dielectric losses to realize non-reciprocal applications at microwave frequencies.

### 4.2 Selection of an Appropriate Hexaferrite Material

The governing property of the materials to be useful for non-reciprocal applications would be their magnetocrystalline anisotropy. Spinel and garnet ferrites are the least preferable for these applications unless the use of bulky and costly permanent magnet is allowed. Their usefulness is further limited by the frequency of operations, which is limited only up to few gigahertz range (~10 GHz). Further, low magnetic anisotropy field and low ferromagnetic resonance frequency (FMR) properties of spinel ferrites and the low saturation magnetization of garnets limit their use in microwave ferrites.

In contrast to the spinel and garnet ferrites, hexaferrites have high magnetic anisotropy field, high FMR and high saturation magnetization. Hexaferrites have proven to be versatile for the applications in the frequency range 1 -100 GHz. There exists a remarkable variation in the types of hexaferrites, which we have already discussed in Chapter 2 (Section 2.4.2, Table 2.3). This Section is concerned with the uniaxial hexaferrites of one of the two groups: $M$-type and $W$-type hexaferrites. The other well-known hexaferrites viz. $Y$ and $Z$-type hexaferrites are not discussed in this Section as they are not preferable for non-reciprocal applications. $Y$ and $Z$-type hexaferrites have their easy axis aligned within the basal plane. These ferrites can be saturated by a small field aligned within the basal plane, while, their magnetocrystalline anisotropy constant ($K_1+2K_2$) is negative. These properties are favourable for the applications in conventional phase shifter, delay lines, filter devices and antenna applications.
Unlike $Y$ and $Z$-hexaferrites, the $M$ and $W$-hexaferrites have their easy axis along the crystallographic $c$-axis. The utility of these hexaferrites stems from the growth of the $M$ and $W$-hexaferrite films with the crystallographic $c$-axis aligned perpendicular to the film plane leads to perpendicular magnetic anisotropy: a requirement for non-reciprocal microwave circulators and isolators$^9$.

**Selecting the correct hexaferrite amongst $M$ and $W$-hexaferrites**

Both $M$ and $W$-hexaferrite system is remarkably versatile in tuning the magnetic properties based on equivalent substitutions for divalent and trivalent metal ions in the given lattice. The important material properties considered for applications in non-reciprocal devices for different substitutions for $M$ and $W$-hexaferrites are given in Table 4.1.

### Table 4.1: Properties of various $W$ and $M$-type hexaferrites$^{8,10,11}$

<table>
<thead>
<tr>
<th>Hexaferrite name</th>
<th>Hexaferrite formula</th>
<th>Magnetization $4\pi M_s$ (Gauss)</th>
<th>Anisotropy field $H_a$ (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$-$W$</td>
<td>BaFe$<em>{18}$O$</em>{27}$</td>
<td>3940</td>
<td>19.0</td>
</tr>
<tr>
<td>Ni$_2$-$W$</td>
<td>BaNi$<em>2$Fe$</em>{16}$O$_{27}$</td>
<td>4145</td>
<td>12.7</td>
</tr>
<tr>
<td>FeZn-$W$</td>
<td>BaZnFe$<em>{17}$O$</em>{27}$</td>
<td>4770</td>
<td>12.5</td>
</tr>
<tr>
<td>FeMnZn-$W$</td>
<td>Ba(MnZn)Fe$<em>{16}$O$</em>{27}$</td>
<td>4650</td>
<td>10.2</td>
</tr>
<tr>
<td>Ba-$M$</td>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>4770</td>
<td>17.0</td>
</tr>
<tr>
<td>Sr-$M$</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>4180</td>
<td>19.0</td>
</tr>
<tr>
<td>Pb-$M$</td>
<td>PbFe$<em>{12}$O$</em>{19}$</td>
<td>-----</td>
<td>13.7</td>
</tr>
</tbody>
</table>

The $W$-type hexaferrites is one of the two hexaferrites with uniaxial magnetic anisotropy and have an *easy-axis* of magnetization in the $c$-axis of hexagonal crystal structure. They have general formula $BaMe_2Fe_{16}$O$_{27}$, where $Me_2$ is divalent metal ions. The structure is constructed as RSSR*S*S*, where S and R are spinel and hexagonal blocks, respectively. The structure is much more complicated as it combines M-type ($Me_2Fe_{16}$O$_{27}$) and Spinel type ferrites within it. The formation of $W$-type hexaferrites does not begin until 1200-1300 °C even with the chemical methods *viz.* co-precipitation, and usually remains with un-reacted spinel phase (*i.e.* multiphase compound) even after such high temperature processing. Further, the material has low bulk resistivity due to the presence of Fe$^{2+}$ ions. Therefore, the $W$-type hexaferrites are not preferred for their utilization in applications, and thus, are not the subject of the investigations in this work.
On contrary, $M$-type hexaferrites offer superior properties than $W$-type hexaferrites. Among $M$-type hexaferrites, strontium $M$-type hexaferrites (SrM) have high anisotropy field and low saturation magnetization than that of barium hexaferrite (BaM). However, the final product of SrM has often been found with Fe$^{4+}$ ions and SrFe$_2$X hexaferrite as a minor product$^{11}$. On the other hand, BaM resembles all properties of SrM at relatively low processing temperature. BaM is remarkably versatile in tuning the magnetic properties based on equivalent substitutions and has been the most explored material for microwave applications in the frequency range 1 to 100 GHz. Further, the realization of the self-biased BaM material will have a wide ranging impact on the development of planar microwave passives leading ultimately towards MMIC integration. Finally, the magnetoplumbite (PbM) have magnetic properties that are inferior to those SrM and BaM, which is self-attestation for the elimination of the material from the potential applications in question.

Keeping the above points in view, BaM hexaferrite has been chosen over the hexaferrite contenders for non-reciprocal application.

### 4.3 Using BaM Material in LTCC

$M$-type barium hexaferrite, BaM, has been intensively investigated throughout the decades, both, due to its fundamental scientific interest and its technological applications. The most explored applications i.e. as permanent magnet and high density recording media are possible due to its large intrinsic coercive field. Simultaneously, BaM exhibit intrinsic high anisotropic field and high ferromagnetic resonance frequency, and thus found applications in non-reciprocal devices at microwave frequencies. The material is usually synthesized by conventional ceramic technique and is formed at 1200 -1400 °C with a known melting point of 1390 °C. The high temperature reaction of the BaM material usually results in very high intrinsic coercivity, which is undesirable for microwave applications. On the other hand, the high temperature processing also limits the use of the material in low temperature co-fired ceramic (LTCC) technology. Both these limitations can be circumvented by the approach described in details in Chapter 2, which are again discussed here in the concise manner to put the subject in proper perspective.

The development of BaM material has been undertaken in this Chapter with the possibility of use of the material to fabricate integrated non-reciprocal devices in LTCC.
Although the device fabrication is beyond the scope of the Thesis, the main objective of the Chapter is to develop compatible BaM material for LTCC technology, with both optimized magnetic properties and very similar sintering profile compatible with LTCC. Both the optimization criteria are treated in the following way:

The principle reasons for favouring BaM material over others for non-reciprocal applications are its intrinsic high anisotropic field (i.e. self-biased property) and ferromagnetic resonance in microwave regions. In addition to these properties, the magnetic properties such as saturation magnetization, coercivity and the remanent magnetization play an important role in the development of these devices at microwave frequencies. Thus, as discussed in Section 4.1 of this Chapter, BaM material designed to have microwave magnetic properties must exhibit moderate/low coercivity, high magnetization, high electrical resistivity, uniaxial anisotropy etc. All these properties are interrelated to each other by one or more controlling factors. For example, the properties like low anisotropy is the one of condition for low coercivity and low loss at microwave frequencies, while, the anisotropy also determines the gyromagnetic resonance frequency of the hexaferrites. While, high saturation magnetization and high bulk resistivity are one of the conditions for high permeability and low losses for the practical use of the BaM material at microwave frequencies. Therefore, one desires an independent control over these properties to customize the material for devices. Similarly, factors such as, crystal size, additives, dopant substitution at equivalent lattice sites control the magnetic properties. Again, there is a need to control these properties, which may be possible during synthesis. Well crystallized BaM material prepared by conventional ceramic technique shows very high coercive field (4500-7000 Oe), making it inapplicable for microwave devices. Thus, in order to use BaM for non-reciprocal applications, the need is to lower its coercivity value and, if necessary, compromise some of the 'high' anisotropy field while continuing to capitalize on this property. Recent reports illustrate that the intrinsic coercivity can be lowered to significant extent by substituting equimolar quantities of divalent (e.g. Ni, Co, Zn) and tetravalent (e.g. Ti, Sn, Ir, Ru, Zr) ions into the trivalent Fe sites. However, these substitutions may, at times, lead to a detrimental effect of reduced saturation magnetization (e.g. CoSn, ZnSn, NiSn etc.) or sometimes lower the coercivity to reasonable extent (~ 2000 Oe), but at the expense of costly substitutions, such as, CoTi. However, these substitutions alter the uniaxial anisotropy to planar anisotropy, which is again undesirable for non-reciprocal applications, as already discussed in this Chapter.
Considering the intricacies between the magnetic properties and synthesis conditions, we revisited the relationship between coercive force and the crystallite size (multi-domain particles give rise to lower coercive field) and applied it in this work to prepare BaM material without any substitutions in the following manner. We have attempted to synthesize the material using one of the established chemical routes as found in the literature to obtain the uniform distribution of particle size with compositional homogeneity in the precursor powder\textsuperscript{14,15}, and, applied the conventional ceramic processing (\textit{i.e.} heat treatment at elevated temperature) to optimize the desired properties through controlled development of multi-domain grains for their use as a microwave ferrites. Accordingly, the solution combustion synthesis is employed in this work (discussed in detail in Chapter 2: Section 2.8.1.2), which favours easy and large-scale synthesis at low cost, and also yields better homogeneity and uniformity in the shape and size of the powder. Thus, the salient aspects of our work on BaM are as follows:

(i) The main objective was to obtain BaM material with an optimum balance of properties for use in integrated non-reciprocal devices at microwave frequencies. In this Section, emphasis is given on obtaining better magneto-structural properties through control of preparation conditions. A combination of synthetic route with different preparation conditions followed by calcination for synthesizing single phase BaM material with optimum electrical and magnetic properties is adapted. The variations in the magnetic and electrical properties are discussed with respect to the preparation conditions by employing various physico-chemical techniques. The optimized powders are further used to study another motive of this work.

(ii) Second motivation was to explore the utility of synthesized BaM material to integrate in LTCC dielectrics. While the part containing its compatibility with LTCC dielectric material is discussed in the Chapter 6, the sintering experiments were performed to study the possibility of sintering BaM at temperatures equal to or below 900 °C without seriously affecting the magnetic properties. This sintering of calcined BaM powder was done at 900 °C with and without sintering aids. The sintering aid used in this study was Bi\textsubscript{2}O\textsubscript{3}, which is a well-known low temperature sintering aid which promotes liquid phase sintering. The study also focuses on characterizing the sintered ferrites using high frequency magnetic characterization and bulk resistivity.
The properties, such as, permeability, loss tangent, resonance frequency and resistivity have been found to study the high frequency properties of BaM hexaferrites.

To realize these objectives, we have attempted to synthesize BaM hexaferrite using solution combustion synthesis which favors easy and large-scale synthesis at low cost, and also yields better homogeneity and uniformity in the shape and size of the powder. The details of this synthesis technique have already been deliberated in Chapter 2. Subsequently, the conventional ceramic processing (i.e. heat treatment at elevated temperature) was applied to optimize the desired magneto-electrical properties through controlled development of multi-domain grains for their use as microwave ferrites. The following Section provides details of this work.

4.4 Synthesis of BaFe_{12}O_{19} Powder Using Solution Combustion Synthesis

4.4.1 Experimental Procedure

A. Powder preparation

The BaFe_{12}O_{19} hexaferrite (BaM) powder was prepared by solution combustion synthesis at two different pH conditions i.e. acidic and neutral of the precursor solution containing metal nitrates and glycine. The solution combustion synthesis was initiated by preparing aqueous solution of the corresponding metal nitrates in stoichiometric proportions. Thus, the analytical grade barium nitrate [Ba(NO_3)_2] and ferric nitrate [Fe(NO_3)_3.9H_2O] were mixed in the Fe/Ba ratio of 12. An aqueous solution of glycine [C_2H_5NO_2] was added as a fuel to the metal nitrate solution in stoichiometric fuel to oxidant ratio to obtain homogeneous solution mixture. Two different pH conditions were employed for synthesis, viz. (1) maintaining the as-prepared, “acidic pH” (termed as acidic precursor solution), and (2) obtaining “neutral pH” (termed as neutral precursor solution) by addition of ammonia solution (min. 25% GR solution). The resultant homogeneous solution mixture was kept in an oven at 100 °C to accelerate the formation of a viscous gel. Finally, the self-propagating combustion of the viscous gel was carried out at 350 °C in an oven for approximately 30 minutes. The resultant powder, thus obtained, was then annealed at 800 and 1200°C, respectively, for different time-temperature cycles with an intermediate grinding after every 3 h. The samples, thus, were prepared for annealing time of 3 hrs, 6 hrs and 12 hrs, respectively. However, it was observed after carrying out the magneto-electrical characterization that the consis-
tent magnetic properties are observed for samples annealed at 800 °C (12 hrs) and 1200 °C (6 hrs and 12 hrs). Hence, the results pertaining to the corresponding these samples are presented in this Chapter.

B. Pellet preparation

In order to study the sintering behaviour of the synthesized BaM, the specimen powder was uniaxially pressed at a pressure up to 100 MPa to fabricate green toroidal (\( \phi_{\text{outer}} = 8 \text{ mm} \); \( \phi_{\text{inner}} = 3.5 \text{ mm} \)) and circular discs (\( \phi = 10 \text{ mm} \)). Prior to compaction, small amount of commercially procured \( \text{Bi}_2\text{O}_3 \) (0, 2 and 4 wt %) was added as a sintering aid in some pellets. The \( \text{Bi}_2\text{O}_3 \) 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 mixture of \( \text{Bi}_2\text{O}_3 \) and the calcined \( \text{BaFe}_{12}\text{O}_{19} \) powder was wet-ground together in an agate mortar and pestle using anhydrous solution of isopropyl alcohol and acetone. The resultant inorganic powder was then blended with 4 wt% polyvinyl alcohol (PVA) to provide strength to pressed green pellets. The green pellets were finally sintered at 900 and 1000 °C with a dwell time of 120 min. in an air atmosphere. The optimized experimental conditions for the samples studied in the current chapter are presented in Table 4.2.

**Table 4.2:** Experimental conditions employed for preparing sintered pellets of combustion synthesized \( \text{BaFe}_{12}\text{O}_{19} \)

<table>
<thead>
<tr>
<th>pH of the precursor sol.</th>
<th>Sample name</th>
<th>Calcination temp. (°C) / time</th>
<th>( \text{Bi}_2\text{O}_3 ) (wt %)</th>
<th>Sintering temp. (120 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>A</td>
<td>800/ 12 h. 1200/ 12 h.</td>
<td>0, 2 &amp; 4</td>
<td>900 &amp; 1000°C</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidic</td>
<td>C</td>
<td>1200/ 6 h. 1200/ 12 h.</td>
<td>0, 2 &amp; 4</td>
<td>900 &amp; 1000°C</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The BaM powder prepared by above methods is subject to various physical, structural and magnetic (property) investigation. Various measurements were performed on powder by using X-ray diffraction technique, Raman spectroscopy (for samples prepared using ceramic route), Mössbauer spectroscopy, field emission scanning electron microscopy and vibrating sample magnetometry. Measurements on pellets include density measurement (Archimedes's method), bulk resistivity, microstructural evolution
and permeability measurements at high frequencies. These measurements were performed on density measurement kit, Keithley electrometer, scanning electron microscopy and Agilent impedance analyzer. The details on instrumentation and characterization conditions are discussed in Chapter 2.

4.4.2 Results and Discussion

In this sub-Section, we will discuss the results on sample characterization by various analytical methods performed on powder specimens followed by property measurements of the pellet samples. The raw BaM powder samples were heat-treated at 800 and 1200 °C to ascertain the optimum/near-optimum magnetic properties with structural integrity of the synthesized powder. The crystal structure of BaFe$_{12}$O$_{19}$ ferrite can be deduced by XRD, while the local lattice co-ordination and symmetry in the synthesized material can be studied by Raman and Mössbauer spectroscopic techniques. Here, it is would be appropriate to give a brief account of crystal structure and symmetry sites of inverse spinel ferrite.

4.4.2.1 Crystal structure of BaM

The crystal structure and behaviour of atoms at the sublattice sites of BaFe$_{12}$O$_{19}$ can be understood by Raman and Mössbauer spectroscopic techniques. Here, it is noteworthy to give a brief account of crystal structure and symmetry sites of BaFe$_{12}$O$_{19}$ hexaferrite. BaFe$_{12}$O$_{19}$ hexaferrite belongs to the class of magnetoplumbite type materials and has a mixed spinel (S and S* blocks) and hexagonal (barium containing R and R* blocks) closed-packed structure, with Ba$^{2+}$ atom substituting for an O$^{2-}$ atom, and iron ion occupying interstices (Figure 4.2). Thus, the unit cell of BaFe$_{12}$O$_{19}$ contains 10 layers of O$^{2-}$ ions, where one oxygen ion in every fifth oxygen plane is replaced by a Ba$^{2+}$ ion. The sequence of the layering in the c-axis direction is RSR*S*, where, R* and S* blocks denote the rotation of the R and S blocks by 180° about the c-axis, respectively. This gives rise to a complex crystal structure of BaFe$_{12}$O$_{19}$, which contains 64 ions per unit cell on 11 different symmetry sites and crystallizes in the P6$_3$/mmc space group. The 24 Fe$^{3+}$ ions exist in five different symmetry sites \textit{viz.} octahedral (12$k$, 4$f_2$ and 2$a$), tetrahedral (4$f_1$) and trigonal bipyramidal (2$b$) sites$^{16,17}$. These sites play an important role in
understanding the magnetic properties of the compound, and are usually studied using Mössbauer spectroscopy. Further, the hexagonal cell of the BaFe\textsubscript{12}O\textsubscript{19} belongs to $D_{6h}^4$ symmetry, in which the irreducible representation of the factor group of 64 atoms in the unit cell of BaFe\textsubscript{12}O\textsubscript{19} may give rise to 42 Raman active modes ($11A_{1g} + 14E_{1g} + 17E_{2g}$), 30 IR-active modes ($13A_{2u} + 17E_{1u}$), and 54 silent modes ($3A_{1u} + 4A_{2g} + 13B_{1g} + 4B_{1u} + 3B_{2g} + 12B_{2u} + 15E_{2u}$), based on the group theory and the Brillouin zone ($k = 0$) conditions\textsuperscript{18}. These modes/ bands belong to the localized vibrations of the polyhedra as discussed above and, have been used for rapid detection and identification of this phase.
Fig. 4.2: (a) The schematic structure of the hexaferrite BaFe$_{12}$O$_{19}$. The arrows on Fe ions represent the direction of spin polarization. The unit cell contains a total of 38 O$^{2-}$ ions, 2 Ba$^{2+}$ ions, and 24 Fe$^{3+}$ ions. Fe$^{3+}$ ions in 12$k$, 2$a$, and 2$b$ sites (16 total per unit cell) have their spins up, while the Fe$^{3+}$ ions in 4$f_1$ and 4$f_2$ sites (8 total per unit cell) have their spins down, which results in a net total of 8 spins up. The R and S subunits shown have chemical formulae $R = (\text{Ba}^{2+}\text{Fe}^{3+}_{6}\text{O}^{2-}_{11})^{2-}$ and $S = (\text{Fe}^{3+}_{8}\text{O}^{2-}_{8})^{2+}$. The asterix (*) indicates that the corresponding subunit is rotated 180 around the hexagonal axis$^{19}$ (b) Polyhedra representation of the BaFe$_{12}$O$_{19}$ crystal structure$^{20}$. 
4.4.2.2 Physical Characterization

A. X-ray diffraction

The powder XRD patterns of the BaFe$_{12}$O$_{19}$ samples prepared by solution combustion technique and annealed at different time and temperatures are shown in Figure 4.3. The diffraction peaks of all the patterns could be identified with the hexagonal structure of BaFe$_{12}$O$_{19}$ in space group P6$_3$/mmc (no. 194), corresponding to the JCPDS reference no. 27-1029.

![X-ray diffraction patterns of BaFe$_{12}$O$_{19}$](image)

**Fig. 4.3**: X-ray diffraction patterns of BaFe$_{12}$O$_{19}$ prepared at different annealing time, temperature and pH values

The XRD patterns do not show any additional diffraction peaks, including those of residual reactants, implying the formation of single phase BaFe$_{12}$O$_{19}$ hexaferrite. This observation is also supported by the Raman spectra of these samples, which is discussed later in this section. Here, it may be noted that as-prepared, fresh-after-combustion material contains undesired phases, as seen from XRD. A calcination step is, therefore, necessary. Further, the samples prepared by an acidic precursor solution were not calcined at 800°C, as one expects inadequate magnetic properties in the samples prepared under these conditions$^{21}$. 
Continuing the structural investigations of the compound, the Raman spectra were studied to further identify the presence of any additional phase or impurity in the synthesized \( \text{BaFe}_{12}\text{O}_{19} \) hexaferrite. Accordingly, the Raman spectra of all samples were recorded in the region of 150 - 800 cm\(^{-1} \) as shown in the Figure 4.4. The laser power operated on the sample was less than 10 mW and the spectral resolution was 0.35 cm\(^{-1} \).

![Raman Spectra](image)

**Fig. 4.4:** Raman spectra of \( \text{BaFe}_{12}\text{O}_{19} \) prepared at different annealing time, temperature and pH values

It is confirmed that all peaks observed in the spectra are indicative of single phase \( \text{BaFe}_{12}\text{O}_{19} \), with no presence of any additional phase or an impurity. Since the illumination power was below 10 mW, no transformation of the compound into other phases or degradation was observed. Accordingly, the peaks observed at 713, and 684 cm\(^{-1} \) can be assigned to \( A_{1g} \) vibrations of Fe-O bonds at the tetrahedral 4\(f_1 \) and bipyramidal 2\(b \) sites, respectively. Other peaks observed at 614, 512, 467, 453 and 317 cm\(^{-1} \) are due to \( A_{1g} \) vibrations of Fe-O bonds at the octahedral 4\(f_2 \), 2\(a \) and 12\(k \) sites, whereas peak observed at 409 cm\(^{-1} \) is due to \( A_{1g} \) vibration at the octahedral 12\(k \) dominated site. The peaks at 527, 285 and 212 cm\(^{-1} \) are due to \( E_{1g} \) vibrations, while peak observed at 335 cm\(^{-1} \) is due to \( E_{2g} \) vibration. The peaks at 184 and 173 cm\(^{-1} \) resulted from \( E_{1g} \) vibrations of the whole spinel block. These characteristic peaks observed in the spectra have been assigned based on the Raman spectral analysis of single crystal \( \text{BaFe}_{12}\text{O}_{19} \) studied by...
Kreisel et al. and Zhao et al\textsuperscript{18,22}. No apparent Raman shifts were observed in these spectra. Therefore, we can infer that the coordinating polyhedra for the Fe ions are present in the lattice of stoichiometric BaFe\textsubscript{12}O\textsubscript{19} in all samples. The assignment of Raman peaks to the corresponding lattice symmetries are summarized in Table 4.3.

**Table 4.3:** Assignment of Raman spectra of BaFe\textsubscript{12}O\textsubscript{19} hexaferrite

<table>
<thead>
<tr>
<th>Raman active modes</th>
<th>Observed frequency (± 3 cm\textsuperscript{-1})</th>
<th>Assigned polyhedra</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>713</td>
<td>Tetrahedra (4f\textsubscript{1})</td>
</tr>
<tr>
<td></td>
<td>684</td>
<td>Bipyramid (2b)</td>
</tr>
<tr>
<td></td>
<td>614</td>
<td>Octahedra (4f\textsubscript{2})</td>
</tr>
<tr>
<td></td>
<td>512, 467, 453</td>
<td>Octahedra (2a + 12k)</td>
</tr>
<tr>
<td></td>
<td>409</td>
<td>Octahedra (12k) dominated</td>
</tr>
<tr>
<td></td>
<td>317</td>
<td>Octahedra 2a</td>
</tr>
<tr>
<td>( E_{1g} )</td>
<td>527, 285, 212</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>184, 173</td>
<td>Whole spinel block</td>
</tr>
<tr>
<td>( E_{2g} )</td>
<td>335</td>
<td>Octahedra 12k</td>
</tr>
</tbody>
</table>

C. Mössbauer spectroscopy

In order to study the local lattice co-ordination and symmetry of iron ions, Mössbauer spectra of all samples were measured at room temperature. Figure 4.5 presents the Mössbauer spectra of samples ‘A’ through ‘D’, fitted using the *WinNormos* fitting program. The hyperfine spectra of all the samples exhibit five overlapping sextets (Zeeman splitting) of iron ions which are assigned according to the structural positions of the magnetoplumbite. This assignment has been done following the model described elsewhere\textsuperscript{23,24}. Accordingly, the sextets have been assigned to the octahedral (12k, 4f\textsubscript{2} and 2a), tetrahedral (4f\textsubscript{1}) and trigonal bipyramidal (2b) iron sites, as shown in Figure 4.4. All lines are assumed to be Lorentzian with the ratio of area for six lines of each of the five sextets to be 3:2:1:1:2:3. The corresponding hyperfine fitting parameters are given in Table 4.4. The spin orientations and the structural subunit, shown in Table 4.4 are taken from the work reported by Gorter\textsuperscript{16}. 

Chapter 4
Fig. 4.5: Mössbauer spectra of BaFe$_{12}$O$_{19}$ prepared at different annealing time, temperature and pH values
Table 4.4: Mössbauer parameters of BaFe$_{12}$O$_{19}$ hexaferrite material

<table>
<thead>
<tr>
<th>pH of the precursor solution</th>
<th>Sample</th>
<th>Iron site and spin orientation</th>
<th>Structural subunit</th>
<th>$\Gamma$ (mm/s)</th>
<th>$\delta$ (±0.02 mm/s)</th>
<th>$\Delta$ (±0.05 mm/s)</th>
<th>$H_{hf}$ (±4.0 kOe)</th>
<th>$R_A$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral 800°C/ 12 h.  (Sample 'A')</td>
<td>$12k \uparrow$</td>
<td>R-S</td>
<td>0.28</td>
<td>0.36</td>
<td>0.41</td>
<td>413.6</td>
<td>44.1</td>
<td></td>
</tr>
<tr>
<td>Neutral 1200°C/ 12 h.  (Sample 'B')</td>
<td>$4f_1 \downarrow$</td>
<td>S</td>
<td>0.29</td>
<td>0.27</td>
<td>0.21</td>
<td>489.4</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_2 \downarrow$</td>
<td>R</td>
<td>0.32</td>
<td>0.37</td>
<td>0.04</td>
<td>511.3</td>
<td>29.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2a \uparrow$</td>
<td>S</td>
<td>0.25</td>
<td>0.41</td>
<td>-0.06</td>
<td>524.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2b \uparrow$</td>
<td>R</td>
<td>0.21</td>
<td>0.28</td>
<td>2.20</td>
<td>400.5</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Acidic 1200°C/ 6 h.  (Sample 'C')</td>
<td>$12k \uparrow$</td>
<td>R-S</td>
<td>0.25</td>
<td>0.36</td>
<td>0.41</td>
<td>414.4</td>
<td>47.4</td>
<td></td>
</tr>
<tr>
<td>Acidic 1200°C/ 12 h.  (Sample 'D')</td>
<td>$4f_1 \downarrow$</td>
<td>S</td>
<td>0.29</td>
<td>0.28</td>
<td>0.20</td>
<td>494.2</td>
<td>27.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_2 \downarrow$</td>
<td>R</td>
<td>0.22</td>
<td>0.38</td>
<td>0.15</td>
<td>516.3</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2a \uparrow$</td>
<td>S</td>
<td>0.14</td>
<td>0.52</td>
<td>0.06</td>
<td>507.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2b \uparrow$</td>
<td>R</td>
<td>0.45</td>
<td>0.24</td>
<td>2.21</td>
<td>402.4</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH of the precursor solution</th>
<th>Sample</th>
<th>Iron site and spin orientation</th>
<th>Structural subunit</th>
<th>$\Gamma$ (mm/s)</th>
<th>$\delta$ (±0.02 mm/s)</th>
<th>$\Delta$ (±0.05 mm/s)</th>
<th>$H_{hf}$ (±4.0 kOe)</th>
<th>$R_A$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic 1200°C/ 12 h.  (Sample 'D')</td>
<td>$12k \uparrow$</td>
<td>R-S</td>
<td>0.26</td>
<td>0.36</td>
<td>0.42</td>
<td>412.2</td>
<td>47.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_1 \downarrow$</td>
<td>S</td>
<td>0.24</td>
<td>0.27</td>
<td>0.22</td>
<td>491.5</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_2 \downarrow$</td>
<td>R</td>
<td>0.24</td>
<td>0.39</td>
<td>0.19</td>
<td>515.9</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2a \uparrow$</td>
<td>S</td>
<td>0.15</td>
<td>0.33</td>
<td>-0.03</td>
<td>510.4</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2b \uparrow$</td>
<td>R</td>
<td>1.14</td>
<td>0.29</td>
<td>2.23</td>
<td>400.9</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>Acidic 1200°C/ 12 h.  (Sample 'D')</td>
<td>$12k \uparrow$</td>
<td>R-S</td>
<td>0.26</td>
<td>0.31</td>
<td>0.42</td>
<td>413.1</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_1 \downarrow$</td>
<td>S</td>
<td>0.20</td>
<td>0.20</td>
<td>0.21</td>
<td>490.7</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4f_2 \downarrow$</td>
<td>R</td>
<td>0.33</td>
<td>0.31</td>
<td>0.04</td>
<td>511.6</td>
<td>38.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2a \uparrow$</td>
<td>S</td>
<td>0.58</td>
<td>0.48</td>
<td>0.32</td>
<td>504.4</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2b \uparrow$</td>
<td>R</td>
<td>0.19</td>
<td>0.24</td>
<td>2.23</td>
<td>400.0</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>
It is observed from Table 4.4 that the hyperfine parameters for all samples are very similar to those found in bulk BaFe$_{12}$O$_{19}$ hexaferrite. It is worthy to note that the hyperfine parameters of sample ‘A’ are very similar to those found in bulk BaFe$_{12}$O$_{19}$ hexaferrite regardless of nano-regime particles (cf. Fig. 4.6A). Thus, the sample ‘A’ does not show superparamagnetic behaviour, as no spin relaxation appears within the Mössbauer characteristic time (~ $10^{-8}$ s). While, sample ‘B’ to ‘D’ contains larger particle (cf. Fig. 4.6B to 4.6D), and thus, a fortiori shows the characteristic of bulk BaFe$_{12}$O$_{19}$ hexaferrite particles. Thus, all Fe spins are magnetically ordered in all samples and do not show any unusual broadening characteristic of superparamagnetic/paramagnetic relaxation effects. All samples exhibit lower hyperfine field ($H_{hf}$) value around 400 kOe and quadrupole splitting ($\Delta$) of 2.20 mm/s for the 2b site, which implies its strongly distorted local lattice environment$^{13}$.

The isomer shift values, $\delta$, of nuclear energy levels with reference to the metallic Fe give the information of the oxidation states and chemical bonding of the sample. It can be observed from Table 4.4 that the $\delta$ values lie in the range of 0.20 - 0.52 mm/s for all five sites, implying an existence of only the high spin, Fe$^{3+}$ cations in all samples$^{25}$. It is known that the isomer shifts and hyperfine fields of Fe$^{3+}$ ions lying within the ‘S’ blocks follow the rule $\delta$ (oct) > $\delta$ (tet) and $H_{hf}$ (oct) > $H_{hf}$ (tet), respectively$^{23}$. It is also expected that the isomer shift of the R-S block octahedral sites would be greater than the spinel tetrahedral sites and similar to the octahedral sites. Considering that the tetrahedral 4f$_{1}$ and octahedral 2a site lie entirely within the ‘S’ subunit and the 12k octahedral site are at the interface of the ‘R’ and ‘S’ subunits (R-S) and that 5 of these sites are derived each from ‘S’ and ‘R’ subunits, the predicted sequence of isomer shifts and hyperfine fields are $\delta$ [2a $\geq$ 12k > 4f$_{1}$] and $H_{hf}$ [2a > 4f$_{1}$], respectively. Next, within the ‘R’ block, where the $\delta$ is proportional to the internuclear separation Fe$^{3+}$-O$^{2-}$, the relative magnitude of the isomer shift between the 4f$_{2}$ and 2a sites is expected to be $\delta$ [4f$_{2}$ > 2a]. Finally, based upon the general correlation between the coordination number and isomer shift for trigonal bipyramidal 2b site (coordination 5) it is expected that the isomer shift of this site would be between 4f$_{1}$ (coordination 4) and 12k (coordination 6) sites, with $\delta$ [4f$_{1}$ < 2b < 12k], although this expectation should be applied cautiously due to the insignificant change in internuclear separation between octahedral and trigonal bipyramidal sites in these compounds$^{23}$. Thus, it is seen from Table 4.4 that amongst the synthesized samples, the disagreement with the
above expectations is seen only for site 2a considering the error in the fitting. It is seen that site 2a shows higher isomer shift than 4f2 for samples ‘B’ and ‘D’. The relatively larger δ corresponds to lower s-electron density at the Fe nucleus and hence may indicate a larger internuclear separation. Further, the hyperfine field shows the trend as found in the bulk BaFe12O19 i.e. \( H_{hf} [4f_2 > 2a > 4f_1 > 12k > 2b] \), except for the sample ‘A’, where a part of it is found to be \( H_{hf} [4f_2 < 2a] \). This may be due to the local inhomogeneity found in the sample ‘A’ as a consequence of fine nature of the particles. In general, the overall good agreement between relative trends in the δ parameter of different sites can be observed regardless of synthesis methods.

D. Field emission scanning electron microscopy

Figure 4.6 (A to D) shows the FESEM micrographs of nanostructured particles in sample ‘A’ with average particle size of 100 nm and irregular hexagonal platelet-structured particles in samples ‘B’ to ‘D’ of size 2-3 μm. Sample ‘D’, however, shows noticeable number of nano range particles below 100 nm as well. It is also evident that samples ‘B’ and ‘C’ contain relatively few particles of size ~ 1 μm or lower, implying the existence of small number of single domain particles amongst largely multi-domain particles. On the other hand, the predominance of single domain particles can be deduced in sample ‘A’ as the critical size for the existence of single domain particles is below 1 μm, as derived by Kittel26. The smaller particle size obtained in the sample ‘A’ is clearly due to the low annealing temperature and its effect on grain growth process.
E. Magnetic Properties/VSM

In order to study the magnetic properties of the synthesized BaM powder material, the \(M-H\) curves at room temperatures were recorded using VSM with a maximum field up to 17.5 kOe. Figure 4.7 presents the hysteresis loops of the samples ‘A’ through ‘D’. The magnetic properties \(\text{viz.}\) saturation magnetization \((\sigma_s)\), remanent magnetization \((\sigma_r)\) and coercivity \((H_c)\) as obtained from the hysteresis loops are listed in Table 4.5. The remanent and specific saturation magnetization is found to be around 30 and 55-60 emu/g, respectively for all samples. These values are in good agreement with those reported in literature for polycrystalline BaFe\(_{12}\)O\(_{19}\)\(^{21,27-29}\), although a higher saturation magnetization has been reported for a single crystal BaFe\(_{12}\)O\(_{19}\) specimen\(^{30}\). The lower saturation magnetization observed in the present samples compared to the single crystal sample, is supported by the Mössbauer spectroscopy results. It is seen that all samples exhibit a large occupancy of Fe\(^{3+}\) ions to the ‘down spin’ sites \(i.e.\ 4f_2\) and \(4f_1\) and a reduced occupancy to the ‘up spin’ \(12k, 2a\) and \(2b\) sites. This may have led to lower number of effective Bohr magnetons \((\mu_B)\), causing a reduction in overall magnetization. Amongst the four types of samples studied here, the samples ‘B’ and ‘C’ show a relatively higher magnetization. This is attributed to the higher occupancy.

Fig. 4.6: FESEM micrographs of BaFe\(_{12}\)O\(_{19}\) powders ‘A to D’ prepared at variable annealing time, temperature and pH values
of Fe$^{3+}$ ions of the ‘up spin’, 12$k$ site relative to the samples ‘A’ and ‘D’. Here, it may be recalled that the number of cations located on 12$k$ : $4f_1 : 4f_2 : 2a : 2b$ sites are 6:2:2:1:1 (per formula unit), and thus, the theoretical areas of the sextets are 50 : 16.7 : 16.7 : 8.3 : 8.3, respectively. These are directly proportional to the number of Fe$^{3+}$ ions in the corresponding sub-lattices. Clearly, variation in occupancy of these sites, usually caused by the processing conditions and the physical form achieved, leads to differences in saturation magnetization.

Table 4.5: Magnetic properties of BaFe$_{12}$O$_{19}$ measured by using VSM

<table>
<thead>
<tr>
<th>pH of the precursor solution</th>
<th>Sample</th>
<th>$\sigma_s$ (emu/g)</th>
<th>$\sigma_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>A</td>
<td>55</td>
<td>29</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>60</td>
<td>30</td>
<td>1350</td>
</tr>
<tr>
<td>Acidic</td>
<td>C</td>
<td>58</td>
<td>30</td>
<td>2046</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>56</td>
<td>31</td>
<td>2420</td>
</tr>
</tbody>
</table>

It is apparent that particle size and morphology may have influenced the $\sigma_s$ and $H_c$ of the samples here. It may be observed that the lowest magnetization is obtained for the sample ‘A’ and ‘D’ with the presence of fine particles and may be understood as arising from intrinsic size effects or surface effects. These properties may give rise to spin non-collinear magnetic structures at the surfaces and consequently the reduction

Fig. 4.7: M-H curves of BaFe$_{12}$O$_{19}$ powders ‘A to D’ prepared at variable annealing time, temperature and pH values
in the magnetization is observed with increase in the surface volume ratio of fine particles\textsuperscript{31}. While, particle size of other samples falls largely in the micro-regime and thus, exhibit a relatively higher magnetization. On the other hand, the coercivity values for sample ‘A’, ‘B’, ‘C’, and ‘D’ vary between 1350 and 3500 Oe, which is significantly lower than the most reported value in literature\textsuperscript{21,27-29}. In multi-domain regime, the coercivity is expected to increase with decreasing particle size\textsuperscript{32}. Here, the pinning of the magnetization occurs at the grain boundaries (which increases with decreasing particle size) causing an increase in coercivity. For the sample ‘A’, where fine grains are observed, the enhanced grain boundaries can act as stronger pinning centers, resulting in a higher coercivity. The coercivity values for sample ‘D’ are intermediate, probably due to intermediate content on nano sized particles. Clearly, the combustion-synthesized BaM material is found to exhibit superior ferrimagnetic properties making this material a potentially useful for integrated high frequency applications.

4.4.2.3 Density and Electrical Characterization

A. Density, Bulk resistivity and Microstructural study of sintered ferrites

Sintering is an essential part of LTCC and ferrite processing alike. Therefore, for any practical use of this ferrite material in LTCC, it is necessary to study the sintering behaviour at about LTCC sintering temperatures and look at the magnetic properties at high frequency. The densification behaviour of the synthesized BaM was studied by sintering the pellets at 900 and 1000 °C with a dwell time of 2 h. and the influence of Bi\textsubscript{2}O\textsubscript{3} and the resultant densification on the electrical properties, viz. the dc resistivity and permeability at UHF-VHF ranges were studied. The sintering density and dc resistivity of the pellets are presented in Table 4.6.
Table 4.6: Sintered density and bulk resistivity of BaFe₁₂O₁₉ hexaferrite samples ‘A’ through ‘D’ as a function of Bi₂O₃ content and sintering temperature

<table>
<thead>
<tr>
<th>Sample name &amp; particle size before sintering [11]</th>
<th>Bi₂O₃ (wt %)</th>
<th>Sintering temp. 900 °C</th>
<th>Sintering temp. 1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Density, (d) (g/cm³)</td>
<td>(d_{\text{bulk}}) (%)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4.72</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.02</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.97</td>
<td>94</td>
</tr>
<tr>
<td>A (~100nm)</td>
<td>0</td>
<td>4.69</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.08</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.88</td>
<td>92</td>
</tr>
<tr>
<td>B (1-2 μm)</td>
<td>0</td>
<td>4.90</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.11</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.08</td>
<td>96</td>
</tr>
<tr>
<td>C (1-2 μm)</td>
<td>0</td>
<td>4.73</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.03</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.14</td>
<td>97</td>
</tr>
<tr>
<td>D (1-2 μm)</td>
<td>0</td>
<td>4.73</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.03</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.14</td>
<td>97</td>
</tr>
</tbody>
</table>
It can be observed from Table 4.6 that the density of pellets without any addition of Bi₂O₃ is significantly high for all samples irrespective of specific preparation condition i.e. about 90% or higher for both the sintering temperatures. With the addition of Bi₂O₃, there is an overall increase in the sintering density of pellets taking it to around 92-97% for all samples. It may be noticed, however, that the density remains in about same range when Bi₂O₃ contents is increased from 2 to 4%, and does not necessarily show an increase. It is felt that the difference is small and does not show any specific trend. Further this difference, which is about 1-3%, is within the experimental variation during sample preparation as well as the error in measurements. The increase in the sintered density due to Bi₂O₃ is expected. This is attributed to the grain growth assisted by the liquid phase sintering caused by Bi₂O₃. It may be noted that Bi₂O₃ has melting point of 825 °C. Such sintering has been reported earlier for known amount of Bi₂O₃ in hexagonal ferrites. Figure 4.8 presents the FE-SEM micrographs of all pellets sintered with 2 wt % Bi₂O₃. It is seen that Sample ‘A’ exhibit platelet particles of size 500 nm, while, sample ‘B’ to ‘D’ exhibit particles in the range of 2 - 6 μm. It is also seen that sample ‘B’ and ‘C’ exhibit uniform grain growth, while, sample ‘D’ exhibit non-uniform distribution of the particles possibly owing to its relatively higher concentration of sub-100 nm particles and large particle size distribution before sintering (Figure 4.6). Overall, it can be concluded that Bi₂O₃ aid sintering of the calcined BaM and promotes its grain growth, resulting in increased sintered density in the range 95%, which can be achieved with only 2 wt% Bi₂O₃ and sintering at 900 °C. In the following part of this Section, the electrical and high frequency magnetic properties of BaM sintered with and without Bi₂O₃, are discussed.
B. Bulk Resistivity

The bulk resistivity of sintered BaM pellets can also be found in Table 4.6. It can be seen that all pellets show resistivity of order $10^9 \, \Omega\cdot\text{cm}$ or more. The high bulk resistivity is due to the presence of predominantly ferric ions in the synthesized compound, which is confirmed by the isomer shift values in the Mössbauer spectra. It is known that the resistivity of ferrite depends on the ferric/ferrous ion content, which aids the electronic conduction of ions distributed randomly over crystallographically equivalent lattice sites\textsuperscript{4}. The range of bulk resistivity obtained for these samples ($10^9 \, \Omega\cdot\text{cm}$) is sufficient to reduce dielectric and eddy current losses at high frequencies, which meets the requirements of RF/ microwave applications\textsuperscript{4,34}. Another noticeable feature is that the samples sintered with Bi$_2$O$_3$ additive exhibit higher bulk resistivity than the samples sintered without Bi$_2$O$_3$ additive. This is could be due to additional grain boundary resistance caused by the presence of Bi$_2$O$_3$ wetting layer between the sintered grains. Such increase in resistance has been found for ferrites sintered with Bi$_2$O$_3$\textsuperscript{33}. Grain boundary effect can also be observed for the pellet of sample ‘A’ and ‘D’ sintered without Bi$_2$O$_3$. Due to lower particle size, the grain boundary resistance is much more pronounced in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_4_8.png}
\caption{FESEM micrographs of BaFe$_{12}$O$_{19}$ pellets ‘A to D’ sintered at 900 °C with 2 wt\% Bi$_2$O$_3$}
\end{figure}

these samples as compared to the other two samples, resulting in about two orders higher bulk resistivity. It may be recalled that sample ‘D’ contains wider grain size distribution with significant number of smaller particles of sub-1 µm as compared to sample ‘B’ and ‘C’. Finally, for samples with micron-sized particles (i.e. sample ‘B’ to ‘D’), the dc resistivity increases with addition of 2 wt% Bi₂O₃ and decreases slightly with increasing amount of Bi₂O₃. On the other hand, samples prepared with nano-sized particles (i.e. sample ‘A’) exhibit the increase in the dc resistivity with the addition of 2 wt% Bi₂O₃ and increases further with 4 wt% Bi₂O₃ addition. This only signifies more pronounced effect of grain boundary resistance due to higher Bi₂O₃ content. This also indicates that there is not much additional grain growth due to additional Bi₂O₃ content in the pellets when the Bi₂O₃ content is increased to 4 wt%.

C. High Frequency Magnetic Characterization

The results of real part (µ') and imaginary part (µ'') of complex permeability obtained as a function of frequency up to 1 GHz are shown in Figure 4.9. One can observe two distinct dispersion regions for the permeability in these sintered ferrites, one being in the lower side of the frequency from 70 to 200 MHz and other on the higher side of the frequency region i.e. above 400 MHz in all sintered ferrites other than sample ‘A’ sintered without Bi₂O₃. The pronounced dispersion region in the sintered BaM samples is attributed to the reversible domain wall displacement in the multi-domain particles. The dispersion above 400 MHz is associated with the resonance of the domain wall as pointed out by Wijn. While, the nature of the dispersion observed on the lower side of the frequency may be attributed to the relaxation process by reasonable part of domain walls, or associated with the resonance frequency by small part of domain walls. Further, the nature of the results is similar to the dispersions found by Wijn, although shifted to the higher frequency range. The dispersion in the frequency found here is between 70 to 200 MHz and 400 MHz to 1GHz, while, Wijn has found the dispersion in the frequency range 20 to 50 MHz and from 200 to 500 MHz.
Looking at the details with respect to the processing conditions, for samples ‘B’ and ‘C’ sintered at 900 °C, the real part of the complex relative permeability ($\mu'$) exhibits the values around 1.7 ± 0.3 up to frequency 100 MHz, and around 1.6 ± 0.1 for the frequency 100 to 500 MHz regardless of Bi$_2$O$_3$ additive. On the other hand, there is distinct difference for samples ‘A’ and ‘D’. The real permeability is distinctly lower for samples with no Bi$_2$O$_3$ content [i.e. A ($\mu'$) - 1.15 and D ($\mu'$) - 1.5±0.1], a fact that is particularly observed for sample ‘A’. Further, the sample A sintered at 900 °C with 2 and 4 wt% Bi$_2$O$_3$ shows relatively lower values around 1.4 ± 0.2 up to 100 MHz, the region where the large variation is observed. The lower $\mu'$ value in the sample ‘A’ and ‘D’ are attributed to the lower grain size obtained in these samples compared to other two sintered ferrites. It may be recalled that particle size in the range of 500 nm was observed for sample ‘A’ and 2-6 μm for sample ‘D’ with significant number of sub-1 μm particles. On the other hand, the grain size in samples ‘B’ and ‘C’ is in the range of 2-6 μm. This difference manifests in higher permeability for these samples. Such dependence of
permeability on the particle size is consistent with the observation by Gieraltowski for series of polycrystalline ferrites\textsuperscript{37}. Further, samples ‘A’ and ‘D’ exhibit markedly lower $\mu'$ values up to 700 MHz when sintered without Bi$_2$O$_3$ in comparison with the samples sintered with 2 and 4 wt% Bi$_2$O$_3$. While, samples ‘B’ and ‘C’ exhibits very small difference in $\mu'$ values when sintered with or without Bi$_2$O$_3$, regardless of sintering temperature. From the sintering density results presented above, it can be concluded that the permeability of the sintered ferrites is a function of sintered density (size and distribution of pores) and average size of the grains. However, it appears that the sample ‘B’ & ‘C’ sintered at 900 °C with 2 wt% Bi$_2$O$_3$ exhibit relatively high permeability together with low coercive field, underling the importance of preparation conditions.

The imaginary part of complex relative permeability ($\mu''$) shown in Figure 4.9 indicates energy loss due to the alternating magnetic field. The $\mu''$ plots for all samples containing Bi$_2$O$_3$ exhibit the higher energy loss than the samples sintered without Bi$_2$O$_3$ in both sintering temperatures. This increase in loss in all samples with the addition of Bi$_2$O$_3$ is attributed to the presence of non-magnetic ions in the samples. On the other hand, sample ‘A’ sintered at 1000 °C without Bi$_2$O$_3$ exhibit much lower energy loss as compared with the sample sintered with 2 and 4 wt% Bi$_2$O$_3$, but the loss is equal in magnitude when sintered at 900 °C without Bi$_2$O$_3$. Overall, the two distinct loss maxima at 120 - 180 MHz and from 650 - 785 MHz can be seen in the $\mu''$ plots which is consistent with the two dispersion regions described earlier.

Figure 4.10 presents the variation in the magnetic loss tangent (tan $\delta$) as a function of frequency. The magnetic losses are below 0.25 at VHF frequencies, while, magnetic losses at UHF vary from 0.2 to 0.5 depending on the sintering temperature and Bi$_2$O$_3$ addition. As seen for the other imaginary permeability plots, both the frequency dispersion regions are conspicuous, and the sintered ferrite exhibits low magnetic losses at the observed frequency ranges. These loss factors are comparative to those reported earliest for this hexaferrite material\textsuperscript{38,39}. In essence, sample ‘B’ sintered at 900 °C with 2 wt% Bi$_2$O$_3$ shows favourable results in terms of high permeability, high resistivity and low losses, underlining the advantage of this synthesized ferrite as a potential substrate material for LTCC RF/microwave applications.
In order to integrate \(M\)-hexaferrite material with LTCC technology, it is necessary that the material to be integrated in LTCC must exhibit chemical as well as physical compatibility. However, it is seen that the paste composed of ferrite material with \(\text{Bi}_2\text{O}_3\) (as a sintering additive and permanent binder) is seen to be incompatible as the warping occurred in the final substrate after co-firing. Therefore, in order to make ferrite compatible with LTCC technology, BBSZ glass was used as sintering aid and permanent binder in the ferrite paste. The results pertaining to the compatibility study are presented in Chapter 6. Simultaneously, it is felt necessary to evaluate the sintering density, bulk resistivity and along with the high frequency permeability results of \(\text{BaM}\) samples in pellet form must be evaluated. Thus, few representative \(\text{BaM}\) samples were evaluated, which were \textit{viz.} Sample B and Sample C. The results are presented below.

**Fig. 4.10:** Frequency dependence of complex permeability of \(\text{BaFe}_{12}\text{O}_{19}\) ferrite for samples - ‘A’ to ‘D’ [\textit{Annotations: Bi}_2\text{O}_3\ in\ wt\% - Sintering temperature]

### 4.4.2.4 Results on M-hexaferrite pellet specimen sintered using BBSZ glass additive

In order to integrate \(M\)-hexaferrite material with LTCC technology, it is necessary that the material to be integrated in LTCC must exhibit chemical as well as physical compatibility. However, it is seen that the paste composed of ferrite material with \(\text{Bi}_2\text{O}_3\) (as a sintering additive and permanent binder) is seen to be incompatible as the warping occurred in the final substrate after co-firing. Therefore, in order to make ferrite compatible with LTCC technology, BBSZ glass was used as sintering aid and permanent binder in the ferrite paste. The results pertaining to the compatibility study are presented in Chapter 6. Simultaneously, it is felt necessary to evaluate the sintering density, bulk resistivity and along with the high frequency permeability results of \(\text{BaM}\) samples in pellet form must be evaluated. Thus, few representative \(\text{BaM}\) samples were evaluated, which were \textit{viz.} Sample B and Sample C. The results are presented below.
The selected M-hexaferrite could be sintered with the help of 2 wt % BBSZ glass in the form of pellets with high value of sintering density (~92-94%). The bulk resistivity for the Sample B and Sample C was in the range of $550 \times 10^9 \Omega \cdot \text{cm}$ and $300 \times 10^9 \Omega \cdot \text{cm}$, respectively, which are comparable values with those obtained in the samples sintered with Bi$_2$O$_3$ content. The permeability spectra also shows similar characteristics discussed earlier in Bi$_2$O$_3$ section. The permeability values are 1.8 up to 100 MHz and sample shows two distinct resonance at 150 MHz and 725 MHz. These values are comparable with the values obtained for the samples sintered with Bi$_2$O$_3$. The corresponding permeability spectra for the Sample B and Sample C are shown in Figure 4.11. Overall, the results are comparable with the results discussed earlier. The preliminary results on the compatibility of the $M$-hexaferrite with BBSZ glass (discussed in Chapter 6) reveal the use of the system for integrated magnetic applications in LTCC.

![Permeability spectra of BaFe$_{12}$O$_{19}$ (for sample B & Sample D) ferrite containing 2 wt% BBSZ glass and sintered at 900 °C for 2 h.](image)

**Figure 4.11:** Permeability spectra of BaFe$_{12}$O$_{19}$ (for sample B & Sample D) ferrite containing 2 wt% BBSZ glass and sintered at 900 °C for 2 h.

### 4.4.3 Conclusions

Here we have shown that single-phase, polycrystalline BaFe$_{12}$O$_{19}$ hexaferrite with necessary structural integrity and compositional homogeneity can be prepared by solution combustion synthesis. The required phase could be formed at low (800 °C) as well as high temperature (1200 °C) conditions. This route allows better control over magnet-
ic properties through change in pH of the precursor solution, and calcination conditions (temperature and duration). The saturation magnetization and coercivity of the calcined powders were 55 - 60 emu/g and 1350 - 3500 Oe, respectively. Compared to the acidic pH condition, the neutral pH of the precursor solution may have appropriate particle size distribution, exhibiting lowest coercivity (1350 Oe) and largest magnetization (60 emu/g) if annealed at 1200 °C for 12 h., which is a prerequisite for RF/microwave applications.

Bi$_2$O$_3$ and BBSZ glass were used as sintering aid to densify the pellets of the BaFe$_{12}$O$_{19}$ hexaferrite at 900 °C. Densely sintered hexaferrites were achieved at this temperature with 2 wt % sintering aid. All samples exhibit excellent sintered density, bulk resistivity and high frequency magnetic properties irrespective of BBSZ or Bi$_2$O$_3$ sintering aids. Detailed analysis using Bi$_2$O$_3$ as sintering aid for the sintered ferrite achieves ~ 95% bulk density, which does not change significantly beyond 2 wt% addition of Bi$_2$O$_3$. Bulk resistivity changes slightly with Bi$_2$O$_3$ content and exhibits the values of order 10$^9$ Ω-cm or more. These resistivity values would results in dielectric losses low enough to meet the requirements of microwave applications. The observed permeability is in the range 1.5 to 2.2 in VHF region, and then decreases to 1.2 in UHF region. The magnetic loss tangent below 0.25 and 0.6 were obtained at VHF and UHF frequencies, respectively. These properties are found to be significantly dependant on particle size, uniformity in grain growth, and influenced by sintering aid up to 2% addition. The sample prepared at neutral pH, calcined at 1200 °C shows maximum densification together with superior electrical and high frequency magnetic properties when sintered at 900 °C with 2% sintering aid (Bi$_2$O$_3$ or BBSZ glass), which can be considered for low temperature cofired ceramic (LTCC) substrate applications at microwave frequencies.
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