CHAPTER – IV
SYNTHESIS OF MATERIAL AND STRUCTURAL ANALYSIS

4.1 Synthesis:

This chapter discusses the different methods of synthesis of materials in bulk form and various experimental techniques used for the characterization. Such techniques involve XRD, SEM and magnetic & dielectric properties and magneto electric (ME) sensing behaviour.

There are several methods available for the synthesis of oxide materials such as ceramic, sol-gel, citrate precursor, combustion, co-precipitation, method etc [1, 2].

The most commonly used method is co-precipitation method. In the present work the different Nitrate materials were synthesized by using co-precipitation method. Apart from this synthesis method, ceramic, sol-gel, citrate precursor, combustion were also been used for the synthesis of nanocrystalline cobalt ferrite.

In the co-precipitation method metal oxides that on decomposition give rise to reactive product are used as precursors. The precursors should be highly pure and in a fine powder form with enough reactivity [3]. The precursors are weighted accurately in required molar proportions.

For chemical synthesis, a precursor compound with an intended stoichiometry is first prepared and is decomposed at temperatures (<873 K) in a subsequent calcination reaction to obtain the required metal oxides [4]. The citrate precursors are usually preferred due to their low solubility, low decomposition temperature and very fine particle nature [5]. Ideally, in order to
achieve a complete reaction within the shortest time and at the lowest possible temperatures, mixing of the component cations on an atomic scale is necessary. Compound precursors achieve this goal, but the stoichiometry of the precursors does not often strictly coincide with the stoichiometry of the desired product [6]. Various authors [7,8] have investigated co-precipitation of metal citrates from appropriately composed solutions in order to produce precursor compounds for spinel ferrites MFe$_2$O$_4$. Wickham [9] has synthesized spinel ferrites MFe$_2$O$_4$ (where M = Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Mn$^{2+}$ or CO$^{2+}$) in air at 873 K.

### 4.1.a Sample Preparation:

The purpose of this work is to use novel and economical method of preparation of Co substituted Ni-Zn ferrites by the citrate precursor method in order to achieve sintering at lower temperatures.

A series of ferrites with composition Ni$_{0.95-x}$Zn$_{0.05}$Co$_x$Fe$_2$O$_4$ and Zn$_{0.95-x}$Ni$_{0.05}$Co$_x$Fe$_2$O$_4$ were chosen for this study. All used reagents were of AR grade. Aqueous solution of stoichiometric amounts of Nickel, zinc, Cobalt nitrates and ferric citrate were reacted with citric acid in 1:1 molar ratio. pH of the solution was increased to 7 by addition of ammonium hydroxide to complete the reaction. The solution was evaporated very slowly over a period of ten to twelve hours to dryness. Viscosity and color changed as the solution turned into puffy, porous dry gel. As soon as the solvent removal is completed, dried precursor undergoes a self-ignition reaction to form a very fine powder known as as-synthesized powder.
Scheme 4.1

Nickel, Zinc, Cobalt nitrates, ferric citrate

Addition of Ammonium hydroxide

Evaporation of solution to dryness

Formation of gel

As synthesized powder

Calcination at 800°C for 2 hrs.

Pelleting / toroids

Final sintering at 900°C – 1200°C

Characterization for magnetic dielectric and electrical

Structural characterization (XRD, FTIR, SEM)
Figure 4.2.1 Process of synthesis of material by co-precipitation

Sintering, Pellet and Toroid Formation:

4.1.b Importance of Sintering:

As material synthesis and processing have become crucial in recent years for materials development, the importance of sintering is increasing as a material Processing technology. Sintering is, in fact, one of the oldest human technologies, Originating in the prehistoric era with the firing of pottery. The
production of tools from sponge iron was also made possible by sintering. Nevertheless, it was only after the 1940s that sintering was studied fundamentally and scientifically. Since then, remarkable developments in sintering science have been made. One of the most important and beneficial uses of sintering in the modern era is the fabrication of sintered parts of all kinds, including powder-metallurgical parts and bulk ceramic components.

Sintering is a processing technique used to produce density-controlled materials and components from metal or/and ceramic powders by applying thermal energy. Hence, sintering is categorized in the synthesis/processing element among the four basic elements of materials science and engineering.

The stage of sintering involves heating of pelletized sample to a high Temperature in air or oxygen. Sintering involves large scale diffusion and erasing of the gradients of chemical potentials, resulting in formation of the final product. In final sintering the rate of sintering must be controlled as it affects the electrical as well as magnetic properties of composites. Controlling the amount of oxygen during sintering favours the formation of good quality composites [10,11]. This increases the density and hence reduces the porosity. The final microstructure together with equilibrium oxygen content and cation distribution depends upon sintering time and temperature [12].

Unlike other processing technologies, various processing steps and variables need to be considered for the production of such parts. For example, in the shaping step, one may use simple die compaction, isostatic pressing, slip casting, injection moulding, etc., according to the shape and properties required
for the end product. Depending on the shaping techniques used, not only the sintering conditions but also the sintered properties may vary considerably. In the sintering step, too, there are various techniques and processing variables; variations in sintered microstructure and properties can result. Sintering aims, in general, to produce sintered parts with reproducible and, if possible, designed microstructure through control of sintering variables. When thermal energy is applied to a powder compact, the compact is densified and the average grain size increases. Microstructural control means the control of grain size, sintered density, and size and distribution of other phases including pores. In most cases, the final goal of microstructural control is to prepare a fully dense body with a fine grain structure.

Sintering must fulfill the following three requirements 1) Bind the particles together so as to impart sufficient strength to the final product. 2) Densify the grain compacts by eliminating the pores. 3) Complete the reaction.

The driving force of sintering is the reduction of the total interfacial energy. The total interfacial energy of a powder compact is expressed as CA, where C is the specific surface (interface) energy and A the total surface (interface) area of the compact.

Here, the change in interfacial energy (DC) is due to densification and the change in interfacial area is due to grain coarsening. For solid state sintering, DC is related to the replacement of solid/vapour interfaces (surface) by solid/solid interfaces. The reduction in total interfacial energy occurs via densification and grain growth, the basic phenomena of sintering. In general,
the size of powders for sintering is in the range between 0.1 and 100 mm; the total surface energy of the powder is 500–0.5 J/mole. This energy is inconsiderably small, compared with the energy change in oxide formation which is usually in the range between 300 and 1500 kJ/mole. If the desired microstructure of the sintered body is to be achieved by the use of such a very small amount of energy, it is necessary to understand and control the variables involved in the sintering processes.

The as-synthesized powder thus obtained was calcinated in a furnace at 800°C for 2 hours to remove the residual carbon. A number of pellets were prepared by weighing a known amount of the powder by pressing them into pellets of 12mm diameter and a thickness of 2mm by applying 5 tones/m weight and made toroids samples for magnetic and electrical analysis. For further studies and finally sintered at 900-1200°C for two hours in air and furnace cooled.

4.2 Characterisation of the Ferro Spinels:

The prepared samples were characterized by using following instruments:

- XRD - .PANalytical Xpertpro Diffractometer
- SEM - JOEL-JSM 6610 LV
- FTIR - BRUKER ALPHA FTIR with Opus 6.1 version
- DC Resistivity – Two Probe Method
- LCR Meter – HP – 4284 and Others
Chemical compositions, structural and textural properties of Ni$_{0.95-x}$Zn$_{0.05}$Co$_x$Fe$_2$O$_4$ and Zn$_{0.95-x}$Ni$_{0.05}$Co$_x$Fe$_2$O$_4$ where $x=0.01$ spinel system ferrites are prepared in the present study are summarized in Table. 4.1

<table>
<thead>
<tr>
<th>NZCF</th>
<th>ZNCF</th>
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<tbody>
<tr>
<td>Ni$<em>{0.94}$Zn$</em>{0.05}$Co$_{0.01}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.94}$Ni$</em>{0.05}$Co$_{0.01}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Ni$<em>{0.95}$Zn$</em>{0.05}$Co$_{0.02}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.93}$Ni$</em>{0.05}$Co$_{0.02}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Ni$<em>{0.92}$Zn$</em>{0.05}$Co$_{0.03}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.92}$Ni$</em>{0.05}$Co$_{0.03}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Ni$<em>{0.91}$Zn$</em>{0.05}$Co$_{0.04}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.91}$Ni$</em>{0.05}$Co$_{0.04}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Ni$<em>{0.90}$Zn$</em>{0.05}$Co$_{0.05}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.90}$Ni$</em>{0.05}$Co$_{0.05}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Ni$<em>{0.89}$Zn$</em>{0.05}$Co$_{0.06}$Fe$_2$O$_4$</td>
<td>Zn$<em>{0.89}$Ni$</em>{0.05}$Co$_{0.06}$Fe$_2$O$_4$</td>
</tr>
</tbody>
</table>

4.3 X-Ray Diffraction Spectral Analysis:

4.3.1 X-Ray Diffractograms (XRD):

X-ray characterization was used for the structural determination of the precipitated powder samples, and the patterns were analyzed and indexed using powder-X software [167]. The lattice parameters were computed using the ’d’ value and the respective (h.k.1) parameters. The calculated lattice parameters ($a_o$) were refined using Powder-X software. One of the most common applications of XRD analysis is to determine the crystal size and the lattice strain of Nanocrystalline materials. The peak broadening patterns in X-ray diffraction of nanomaterials which is the result of the finite size effect. Nanocrystal to a finite size, the number of X-ray radiation reflected from successive lattice planes which are summed to produce a constructive or destructive interference becomes finite and therefore cannot reinforce or cancel completely. Additionally, some other factors such as the inhomogeneous lattice strains, variations in the lattice constants of a crystallite and other structural faults can also cause broadening of diffraction peaks.
The size of nanomaterials can be derived from the peak broadening and calculated using the Scherrer equation, provided that the nanocrystalline size is less than 100 nm.

\[ d = \frac{K\lambda}{\beta \cos \theta} \]  

(4.1)

where \( d \) is half the dimension perpendicular to the crystalline phases reflecting, \( \lambda \) is the x-ray wavelength, \( \theta \) is the Bragg angle, and \( \beta \) is the broadening of finite size. \( K \) is a constant near unity which is related both crystalline form and \( \beta \) as defined manner, ie either as the full width at half maximum (FWHM) or as the full width i.e. the peak area ratio to peak.

Figure 4.2.2-6 shows a typical XRD pattern for samples sintered at 800°C. The pattern shows all the characteristic peaks of a spinel structure and confirms the phase formation indicating the absence of other impurity phases. The lattice parameters were calculated using XRD data and it is observed that there is a compositional variation in lattice parameter. The lattice parameter for all the Co-substituted Ni–Zn ferrites increase with increasing Co content, which can be attributed to the larger ionic radius of \( \text{Co}^{2+} \) (0.78 \( \text{Å} \)) than \( \text{Ni}^{2+} \) (0.74 \( \text{Å} \)). The linear variation of the lattice parameter with respect to Co concentration fulfills the condition of Vegard’s law. Data on average crystallite size of sintered powder determined by x-ray diffraction using the Debye–Scherer formula for the Co-substituted Ni–Zn ferrites is given in table 4.2.1&4.2.2.

It can be seen that for small amounts of Cobalt incorporation there is a sharp and significant decrease in particle size while for higher concentration of
Cobalt, the decrease in particle size is less pronounced. It may be noteworthy that Arulmurugan et. al. [10] noticed a linear trend in the variation of particle size and lattice parameter of nano sized Ni-Zn mixed ferrites. It is to be construed here that an increase in Cobalt concentration in the solution during synthesis increases the reaction rate which favours the formation of ultrafine particles of mixed ferrites. The difference in average particle size between the extremes (for x=0.01 and x=0.02) was found to be approximately 20nm which is quite significant. This accounts the role of Cobalt substitution in reducing the particle size of the series.

The lattice parameter of all the compositions in the series Ni-Zn mixed ferrites was evaluated after assuming cubic symmetry. The variation of lattice parameter with Cobalt concentration is depicted in figure 4.2.1 &4.2.2. A similar type of variation is also observed in bulk Mn_{1-x}Zn_xFe_{2}O_{4} which is attributed to the substitution of bigger sized Ni^{2+} cations (0.091nm) by Zn^{2+} cations having smaller radii (0.082nm) for bigger. However a relative contraction of the lattice is observed with respect to bulk for the same composition(x) [11]. In the case of bulk Ni-Zn ferrite, the presence of Ni2+ and Ni^{3+} ions and the volatilization of Cobalt were believed to be contributing to the contraction of the lattice [12]. However, chances of Cobalt evaporation are virtually nil since the methods adopted for the synthesis are based on co-precipitation techniques. But the chances of formation for the formation of Ni^{3+} cations during the precipitation process-cannot be ruled out since Ni^{3+} is easily oxidized in a highly basic solution [13]. Since Ni^{2+} ion has a preferential
occupancy for octahedral geometry, it may be accommodated in the B site. In the process, in order to maintain charge neutrality of the B Site, some Fe$^{3+}$ ions may be converted into Fe$^{2+}$ ions. The presence of Ni$^{2+}$ and Fe$^{2+}$ in octahedral site can result in the JahnTeller distortion of the octahedral symmetry of B sites which might lead to a lattice distortion in these mixed ferrites. This type of lattice distortion was observed in co-precipitated manganese ferrite nanoparticles [13].

<table>
<thead>
<tr>
<th>S No</th>
<th>Sample</th>
<th>Lattice Parameter</th>
<th>Density (%)</th>
<th>FWHM</th>
<th>Porosity (%)</th>
<th>Grain size(D) (μm)</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>8.387</td>
<td>92.5</td>
<td>0.281</td>
<td>7.4</td>
<td>1.62</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>8.389</td>
<td>91.9</td>
<td>0.272</td>
<td>7.3</td>
<td>1.58</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
<td>8.392</td>
<td>91.7</td>
<td>0.228</td>
<td>6.8</td>
<td>1.46</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>8.395</td>
<td>92.2</td>
<td>0.260</td>
<td>8.0</td>
<td>1.41</td>
<td>22</td>
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<tr>
<td>5</td>
<td>0.05</td>
<td>8.396</td>
<td>92.5</td>
<td>0.249</td>
<td>8.3</td>
<td>1.39</td>
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</tr>
<tr>
<td>6</td>
<td>0.06</td>
<td>8.398</td>
<td>93.5</td>
<td>0.280</td>
<td>7.7</td>
<td>1.36</td>
<td>22</td>
</tr>
</tbody>
</table>

**Table 4.2.1. Structural variation of NZCF**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter</th>
<th>Density (%)</th>
<th>FWHM</th>
<th>Porosity (%)</th>
<th>Grain size(D) (μm)</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>8.387</td>
<td>92.6</td>
<td>0.279</td>
<td>7.1</td>
<td>1.618</td>
<td>28</td>
</tr>
<tr>
<td>0.02</td>
<td>8.389</td>
<td>93.4</td>
<td>0.276</td>
<td>7.0</td>
<td>1.60</td>
<td>27</td>
</tr>
<tr>
<td>0.03</td>
<td>8.392</td>
<td>91.7</td>
<td>0.232</td>
<td>6.1</td>
<td>1.52</td>
<td>22</td>
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<tr>
<td>0.04</td>
<td>8.395</td>
<td>90.9</td>
<td>0.255</td>
<td>7.8</td>
<td>1.45</td>
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<tr>
<td>0.05</td>
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<td>92.5</td>
<td>0.251</td>
<td>8.1</td>
<td>1.405</td>
<td>21</td>
</tr>
<tr>
<td>0.06</td>
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<td>92.9</td>
<td>0.275</td>
<td>7.9</td>
<td>1.38</td>
<td>21</td>
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</table>

**Table 4.2.2. Structural variation of ZNCF**

From table 4.2.1 and 4.2.2, it is seen that the average crystallite size for the sintered powder of different compositions of Ni–Co–Zn ferrites is found to be in the range of 25–28 nm. The values of crystallite size evaluated from XRD
(FWHM) are in agreement with those reported by Parvatheeswara Rao et al [11].
Figure 4.2.2 XRD Spectral Patterns of the Nanoferite
The crystallinity and structure of the precursors calcined at 800°C were confirmed by powder X-ray diffraction. Fig. 4.2.2 shows X-ray diffraction patterns measured at different Zn-content. The peak position and relative intensity of all diffraction peaks match well with standard powder diffraction data (JCPDS file No.: 08–0234) and no impurity peak was observed, which indicated that high purity crystalline Ni\(_1-x\)ZnxFe\(_2\)O\(_4\) system with cubic spinel structure was synthesized. The peaks can be indexed to (111), (220), (311), (222), (400), (422), (511) and (440) planes of a cubic unit cell.

**4.3.b FT-IR spectroscopy**

In the range 4000–400 cm\(^{-1}\), the IR bands of solids are usually assigned to vibration of ions in the crystal lattice. In order to confirm the formation of the spinel phase and to understand the nature of the residual carbon in the samples, the FTIR spectra of the as-synthesized powders and thermally treated powder were recorded, Figure (4.2.2). The as-synthesized sample shows characteristic absorptions of ferrite phase with a strong absorption around 600 cm\(^{-1}\) and weak absorption in the range 410-450 cm\(^{-1}\)[8]. This difference in the band position is expected because of the difference in the Co\(^{2+}\) distance for the octahedral and tetrahedral compounds. Waldron [10] studied the vibrational spectra of ferrites and attributed the sharp absorption band around 600 cm\(^{-1}\) to the intrinsic vibrations of the tetrahedral groups and the other band of the octahedral groups. In the Ni-Zn solid solutions, for NZCF Ni\(^{2+}\) is stabilized in the octahedral crystal fields where as Co\(^{2+}\) prefers octahedral sites replacing Ni and some Fe\(^{3+}\) are forced to migrate from B to A site. For NZCF, Zn\(^{2+}\) is
stabilized tetrahedral crystal field where as Co$^{2+}$ prefers octahedral field because of its facility to form covalent bonds involving Sp3 hybrid orbitals.

There are two weak and broad absorptions around 1400 and 1600 cm$^{-1}$ corresponding to the presence of small amount of residual carbon in the samples. These absorptions in the present case are very weak which indicate that the residual carbon has mostly burnt away during the sintering process.

![FTIR spectrum](image-url)

**Figure 4.2. 2** FTIR spectra of the Nanoferrite

**4.3.c Surface Morphology (SEM):**

The SEM micrographs of Cobalt substituted Ni-Zn ferrite samples containing Cobalt content of $x = 0.01$ to $0.06$ are shown in Fig 4.2.3 sintered at 800c. The average grain size was calculated by the line intercept method. It is
clear from the figures that the particles have well-defined shape and boundaries. In view of the fact that the crystallite sizes calculated by the Scherer formula are not considered being very accurate therefore we have recorded the SEM images of some of the synthesized samples. It is observed that the average grain size decreases with the addition of cobalt, as tabulated in table 4.2.1 & 4.2.2 for NZCF and ZNCF. It is seen that, as x increases, the grain size decreases appreciably. The values of particle sizes calculated by SEM found to be 40–90 and 30–50 nm, respectively for the samples with Cobalt content of x = 0.01 to 0.06. The particle sizes for the samples synthesized in the present study are much smaller as compared to those of the reported earlier 83, 151–200, 70–100 and 60–300 nm for the M-type hexa ferrite [28–30]. These particle sizes are small enough to obtain the suitable signal-to-noise ratio in the high density recoding media. The synthesized samples can be therefore used for application in recoding media.
Figure 4.2. SEM micrograph of the Cobalt Substituted Nickel Zinc Ferrites

Figure 4.5 shows micrographs of powder observed by SEM. The powder is composed by nanoparticles. The crystalline phases of Ni-Fe alloy and iron oxide were identified by XRD analysis. On the other hand, the Ni Zn ferrite crystalline phases like found under argon/air/vacuum atmosphere were not determined by XRD, on the powder of this work. Probably, one explanation for that is zinc evaporated during calcinations process and/or became an amorphous.

4.3.d Scanning Electron Microscope Analysis:

Scanning electron micrograms of calcined samples showed particles of size in the range 49 nm, which confirm the crystalline nature of the material. Thus the crystalline nature of the material, as revealed from the XRD data, is supported by SEM images.
This analysis involving the above spectral data shows that spinel structures have been obtained by this chemical route at lower temperatures. This method is time saving when compared to the time consuming and tiresome processes involved in the manufacturing of nano ferrites.

The powder synthesized by the citrate precursor method demonstrated considerable sinterability. The fine particle morphology of the powder synthesized by this method is responsible for its higher sintering activity. Obtaining single phase ferrite directly from the citrate precursor without any additional heat treatments is a significant achievement, considering the variety of applications of Ferrites and substituted ferrites. The highly active powders can be sintered at relatively low temperatures to obtain highly dense and homogeneous polycrystalline ferrites for high frequency applications.

Since, spinel ferrites have been the subject of great interest for the past five decades, because of their wide range of applications in transformers, inductors, choke coils, noise filters magnetic recording heads, and so forth [1]. These ferrites possessing cubic close-packed structure of oxygen ions, are described by the formula \((A)[B]_2O_4\), where \((A)\) and \([B]\) represent tetrahedral and octahedral sites, respectively. The site occupancy is often depicted in the chemical formula as \((M_{1-\delta}Fe_\delta)[M_\delta Fe_{2-\delta}]O_4\), where round and square brackets denote the A- and B-sites, respectively, \(M\) represents a metal cation, and ‘\(\delta\)’ is the inversion parameter. The degree of inversion ‘\(\delta\)’ for spinel ferrites is defined as the fraction of tetrahedral (A)-sites occupied by trivalent cations. Accordingly, for a normal spinel \(\delta = 0\) and for a completely inverse spinel, \(\delta = \)
1. The magnetic and the electronic properties of such a ferrite system depend upon the type of metal cations and their distribution among the two interstitial sites, that is, A- and B-sites. Therefore, the knowledge of cation distribution is essential to understand the magnetic behavior of spinel ferrites. Manganese ferrite is early known to be a mixed inverse spinel, and the degree of inversion mainly depends upon the method of preparation. The presence of nonmagnetic ions in these spinel ferrites is found to alter their magnetic and electronic properties. The addition of metal cations such as trivalent or tetravalent influences the electronic and magnetic properties of the ferrite system [2–6]. Various studies showed that heating might change the distribution of metal cations at the A- and B-sites of CoFe$_2$O$_4$. It has been reported that by using neutron diffraction technique, the degree of inversion, that is, the distribution of the cationic ions between the tetrahedral and octahedral sites of CoFe$_2$O$_4$ prepared by usual ceramic route was determined 81% normal [7]. However, this value reduced to 33%, when CoFe$_{0.9}$O$_4$ was prepared by wet chemical method [8]. Thus, the method of preparation may play a crucial role in order to obtain the desired electronic and magnetic properties.

Further investigations in this direction are going to help in understanding the properties of Cobalt substituted Ni Zn Ferrites.
References