Recent developments in processing of Mn – Zn ferrites—An overview

C E Deshpande & S K Date
Physical Chemistry Division, National Chemical Laboratory, Pune 411 008

Introduction

Mn – Zn ferrites belong to a category of soft ferrites which are ferrimagnetic oxides with spinel structure having low coercivities. They are technically important materials because of their high magnetic permeability and low core losses. These ferrites have been used for several decades as magnetic cores in high frequency coils and transformers. There has been a continuous increase in magnetic permeability and decrease in magnetic losses in ferrite materials leading to improved performance over years (Fig. 1). The soft ferrites are widely used in telecommunication devices and entertainment electronics applications as summarized in Table 1. During the last decade, Mn – Zn ferrites were used in the frequency range of about 16-25 kHz. However, with the emergence of switched-mode power supply very rapid development of high frequency ferrites (power ferrites) was seen in electronics industries. Frequency operation increased rapidly and power-supplies operating at 1 MHz and above were commercially available by 1990. Demand for compact power supplies increased due to the computers, microprocessors and VCR systems which enhanced the market for power ferrites. Ruthner has estimated total world soft ferrite production in metric tonnes per year (MTPY) along with the consumption of iron oxide for their production (Table 2). As per the estimates, total ferrite production in India was around 9000 MTPY in 1989 which included 3000 MTPY of soft ferrite.

Keeping in view the scientific and technical importance of Mn – Zn ferrites, we have attempted to review some of the recent developments on processing of this important electronic ceramic material along with its basic background.
Table 1—Summary of Mn—Zn ferrite applications²

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Device</th>
<th>Frequencies</th>
<th>Desired ferrite props.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Inductor</td>
<td>&lt;1 MHz</td>
<td>High (\mu), high (\mu_Q), high stability of (\mu) with temp. and time.</td>
</tr>
<tr>
<td>2.</td>
<td>Transformer (Pulse and wide band)</td>
<td>Up to 500 MHz</td>
<td>High (\mu), low hysteresis losses</td>
</tr>
<tr>
<td>3.</td>
<td>Loading coil</td>
<td>Audio</td>
<td>High (\mu), high (B), high stability of (\mu) with temp. and time and dc bias.</td>
</tr>
<tr>
<td>4.</td>
<td>Flyback transformer</td>
<td>&lt;100 kHz</td>
<td>High (\mu), high (B), low hysteresis losses.</td>
</tr>
<tr>
<td>5.</td>
<td>Deflection yoke</td>
<td>&lt;100 kHz</td>
<td>High (\mu), high (B).</td>
</tr>
<tr>
<td>6.</td>
<td>Suppression bead</td>
<td>Up to 250 MHz</td>
<td>Mod. high (\mu), high (B), high hyst. losses.</td>
</tr>
<tr>
<td>7.</td>
<td>Choke coil</td>
<td>Up to 250 MHz</td>
<td>-do-</td>
</tr>
<tr>
<td>8.</td>
<td>Recording head</td>
<td>Up to 10 MHz</td>
<td>High (\mu), high density, high (\mu_Q), high wear resistance.</td>
</tr>
<tr>
<td>9.</td>
<td>Power transformer</td>
<td>&lt;60 kHz</td>
<td>High (B), low hyst. losses.</td>
</tr>
</tbody>
</table>

Table 2—Estimated world ferrite production⁴

<table>
<thead>
<tr>
<th>Year</th>
<th>1990</th>
<th>1995</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total ferrite production (MTPY)</td>
<td>516,000</td>
<td>665,500</td>
<td>974,000</td>
</tr>
<tr>
<td>2. Soft ferrite production (MTPY)</td>
<td>150,000</td>
<td>185,500</td>
<td>221,500</td>
</tr>
<tr>
<td>3. Fe₂O₃ consumption for soft ferrite (MTPY)</td>
<td>105,000</td>
<td>130,000</td>
<td>155,000</td>
</tr>
</tbody>
</table>

2 Theoretical Background

Crystal structure

Mn—Zn ferrite has a cubic spinel structure (Fig. 2a). It consists of a typical face-centred cubic structure of oxygen ions with two types of lattice/crystallographic sites—tetrahedral (A) and octahedral (B)—available for metal ions. Fig. 2b shows the configurations of the ion pairs in the spinel lattice for which the distance and angles are most favourable for different types of lattice site interactions⁶. The unit cell of the spinel is represented by \(\text{M}^{II}\text{Fe}^{III}\text{O}_3\). Thus, there are eight formula units of \(\text{M}^{II}\text{O} \cdot \text{Fe}^{III}_2\text{O}_3\) (MFe₂O₄) in a unit cell (M⁰ representing the divalent ions such as Mn²⁺ and Zn²⁺ in case of Mn—Zn ferrite). The site occupancy of an ion depends on its site preference energy⁷, which in turn is temperature dependent. In addition, the occupancy of a particular lattice site depends on thermal history of the spinel, i.e., the high temperature structure is frozen during quenching while in slow cooling, sufficient time is available for the readjustment of ions to the equilibrium configuration.
Magnetic interactions

Magnetic interaction between the two atoms of spins $S_i$ and $S_j$ is given by

$$E = -2J_e S_i \cdot S_j \quad \ldots \quad (1)$$

where $J_e$ is the exchange integral and is a measure of the extent of overlap of the electronic charge of the two atoms. This direct exchange interaction may be either positive or negative depending upon the ratio of atomic separation ($D$) to the diameter of $d$-orbit ($d$), i.e., $D/d$. For $D/d < 1.5$, the exchange interaction is negative, attains maximum value at $D/d = 1.8$ and subsequently diminishes to a very small but positive value of $D/d = 3$ (Fig. 3). In ferrimagnetic spinels $D/d = 2.5$, indicating weak positive interaction by direct exchange. However, experimental evidence favours a strong negative $A-B$ interaction in spinel ferrite which accounts for the experimental magnetic moment value which is drastically different from the value calculated on the basis of positive ferrimagnetic $A-B$ interaction. The mechanism by which the negative $A-B$ interaction is obtained via the intervening oxygen ions known as 'superexchange' has been suggested by Anderson. This mechanism results in a negative interaction favouring antiferromagnetism when the $d$ orbitals of the metal ions are half-full or more than half-full, while a positive interaction accompanied by ferromagnetism results when the $d$ orbital is less than half-full. The mechanism may be explained in brief as follows. The electrons in the outermost shell of $O^{2-}$ are paired and occupy $p-\sigma$ and $p-\pi$ orbitals. The $O^{2-}$ is diamagnetic but an excited state is possible in which an electron from $p-\sigma$ orbital of $O^{2-}$ is transferred to one of the neighbouring $Fe^{3+}$ ions which momentarily becomes $Fe^{2+}$ ion. The transient oxygen ion becomes paramagnetic because of its unpaired electrons. Its moment can have direct exchange with the moment of other $Fe^{3+}$ ions.

The superexchange may also involve $p-\pi$ orbitals which have positive overlaps with the $t_{2g}$ orbitals of the metal ions, while $p-\sigma$ have stronger overlaps with $e_g$ orbitals of the metal ions. $p-\pi$ with $e_g$ or $p-\sigma$ with $t_{2g}$ give negative overlaps. Therefore, in ferrites the result of the indirect exchange through oxygen is a net antiferromagnetic interaction between any two transition metal ions. This mechanism predicts a strong antiferromagnetic interaction when the metal-oxygen-metal ($M-O-M$) angle is 180° and also where the interatomic distance is the shortest. A weaker interaction exists when this angle is in the neighbourhood of 90° and the interatomic distances are too large. In a spinel structure, the $AOB$ angle is in the neighbourhood of two right angles while the $AOA$ and $BOB$ angles are closer to one right angle. One should expect, therefore, a very strong $AOB$ antiferromagnetic interaction which dominates and virtually suppresses the weaker $AOA$ and $BOB$ antiferromagnetic interactions. One should thus expect the metal ions on $A$ sites to be aligned parallel to one another as also those on $B$ sites, while the net moments at the $A$ and $B$ sites should align antiparallel to one another. A model based on ferrimagnetism was proposed to account for the observed magnetic moments of ferrites by Neel. It is the basis of our present understanding of the various types of magnetic interaction occurring in spinel lattice.
Magnetic properties and performance parameters

The magnetic properties/performance parameters of soft ferrite magnet are best understood with the help of its hysteresis loop [Fig. 4(a)]. The area of the hysteresis loop is a measure of the magnetic losses that take place during the magnetization processes. The value of magnetic induction (B) at applied magnetic field (H) = 0 on the demagnetization curve is called the remanent induction or remanence (B_r) and the value of the reverse field applied to reduce the magnetic induction (B) to zero is called the coercive force or coercivity (H_c). They are expressed in units of Gauss and Oersteds respectively. Both these parameters are very important from application point of view of ferrites.

Initial permeability (μ_i)—The magnetic permeability (μ) is the ratio of magnetic induction B to the magnetizing field H. This parameter can be measured under different sets of conditions, e.g., if the magnetizing field is very low, approaching zero, the ratio of B/H is called initial permeability μ_i, μ_i = limit (B/H) as H→0. With increasing H, permeability (μ) increases to a maximum value μ_max and then decreases again as B gets saturated and attains the value B_s. The parameter μ_s is one of the most important parameters for telecommunication applications of soft ferrites.

Crystal anisotropy and permeability—An unmagnetized ferrite material consists of a large number of small domains with parallel spins in individual domains called Weiss domains. These domains are oriented in all possible directions and the resulting magnetic moment is zero. A transition zone exists between two adjacent domains in which the orientation of domains is gradually changed. This zone is called a Bloch wall. During the magnetization with a large magnetic field, all domains are oriented in the direction of applied magnetic field. The orientation can take place either by rotation of domains or by wall displacements as shown in Fig. 4b (ref. 12a). It shows the processes taking place in the three different regions of the curve for magnetization of the virgin specimen. The first is the lower section of the curve characterized by reversible domain wall displacements or domain rotations. It means that after changing the magnetization slightly (by increasing the applied field) the original magnetization condition can be returned if the field is reduced to the original value. The second stage of the magnetization curve is one with increasing slope in which irreversible domain wall displacement takes place. The third section of the curve is one of irreversible domain rotations with a flat slope indicating the large amount of energy that is required to rotate the domain magnetization in the direction of H. In ferrites, magnetization takes place preferably by domain rotations since the Bloch walls are more difficult to move due to voids present in the material. However, it is clear from Fig. 4 (a&b) that initial permeability μ_i is due to the domain wall displacement and not due to domain rotation. Thus, large μ_s is primarily associated with low crystal anisotropy in Mn-Zn ferrites and attains maximum value as the crystal anisotropy K approaches zero. This is achieved by introducing a small calculated amount of Fe^3+ ions which contributes a positive anisotropy. Mn-Zn ferrite has a negative crystal anisotropy which makes the resultant K = 0.

Magnetostriiction and permeability—Another important factor that affects the permeability is magnetostriiction (λ), which is a change in mechanical shape of a magnetic material on magnetization. Conversely, a magnetization is caused by changes in shape by means of internal stresses. This preferred direction of magnetization in the direction of stress lowers the permeability. Magnetostriiction can be minimized by making mixed crystals of cubic ferrites having negative and positive magnetostrictions. It is reported that the compositional dependence of the permeability is interpreted from those of crystal anisotropy (K), magnetostriction (λ) and Curie temperature (T_c). High permeability (μ_i) and minimum loss factor (tan δ/μ) were found for the composition range corresponding to K = 0 with minimum magnetostriction (λ). Fig. 9 shows the phase diagram which clearly indicates the region of ferrite compositions with μ_max and the regions were desirable magnetic properties can be optimized.

Shape anisotropy and permeability—Shape anisotropy is created in the ferrite by the presence of nonmagnetic second phase present as an impurity or even due to voids filled with air. These impurities result in incomplete magnetic circuit in the material causing a demagnetizing field. Permeability is lowered due to the preferred orientation in the direction of demagnetizing field.

Magnetic losses

When a magnetic material is employed as a core material for a high frequency transformer some energy gets dissipated as heat-energy which is termed as core losses. For soft magnetic materials used in low power transformer cores losses are described in terms of complex permeability at low field strengths. Permeability μ separates into μ' and μ", which are related as μ = μ' - iμ".
These are governed by anisotropy and magnetostriction. Therefore, the temperature-dependent properties of ferrites, namely, Fig. 5—Crystal anisotropy (K) and permeability (μ) as a function of temperature (T), of an extremely homogeneous MnZnFe²⁺ ferrite\(^{11}\).

where \(\mu'\) represents the component of B in phase with H (real permeability), while \(\mu''\) refers to the part of B which is 90° out of phase with H (imaginary permeability). The loss tangent is given by \(\tan \delta = \mu''/\mu'\) where \(\delta\) is the loss angle of the core material and the inverse of \(\tan \delta\) is quality factor \('Q'.\) Normalised loss tangent per unit of permeability i.e. \(\tan \delta/\mu\), represents the 'Loss factor' (LF).

The losses in magnetic material are classified into three groups: (1) eddy current losses, (2) hysteresis losses and (3) residual losses. The eddy current loss factor is proportional to \(d^2f^2/\rho\), where \(d\) is the smallest dimension of the material, \(f\) the frequency and \(\rho\) the resistivity. In metal magnets, this is the prominent loss factor contributing to the core losses. However, in ferrites the eddy current is normally negligible because of high \(\rho\), though in Mn–Zn ferrite resistivity is low due to its Fe\(^{2+}\) ion content resulting in higher losses at high frequencies. The hysteresis loss per cycle is proportional to the area of the B–H loop of the ferrite material [Fig. 4(a)]. At high magnetic fields (H) and high magnetic induction (B) values, these losses become very prominent and are measured in watts/cm\(^3\). For high field applications, the heat developed in the core becomes more important than LF alone since it contributes to the total losses of the material. The residual losses are usually negligible for metallic core materials, but in ferrite cores these losses constitute the major part of \(\tan \delta/\mu\) at low fields.

**Temperature factor** (TF) of permeability

Permeability of a ferrite is the result of intrinsic and extrinsic effects acting simultaneously on it. These are governed by the chemistry and structure-dependent properties of ferrites, namely, anisotropy and magnetostriction. Therefore, the permeability variation with temperature depends on many parameters that are temperature-dependent in themselves. We see a wide variation in the shape of the permeability versus temperature curve (Fig. 5) for the high permeability Mn–Zn ferrite\(^ {13}\). The permeability rises and attains a maximum at a temperature little before the Curie temperature (\(T_c\)) since the exchange energy, the anisotropy and internal stress all decrease due to heating. This maximum (peak) drops to zero at the Curie point since the ferrimagnetism is lost.

For Mn–Zn ferrite, one more peak called the secondary maximum of permeability (SMP) occurs close to the temperature at which the crystal anisotropy (K) goes through zero. This peak can be moved to the temperature at which the ferrite is to be used by varying its chemistry and changing the shape of \(\mu-T\) curves\(^ {14}\). SMP is normally adjusted to be in the temperature region of operations, i.e., 60 to 100°C for optimum use of the ferrite material. The temperature factor (TF) of permeability is calculated as \(1/\mu\cdot d\mu/dT\) which is a material constant\(^ {15}\) useful to predict the variation in magnetic properties of a magnetic component. TF can be brought down by introducing an air gap in the magnetic circuit\(^ {16}\).

**Disaccommodation factor** (DF)

The disaccommodation of Mn–Zn ferrite is an ageing effect indicating the fall in permeability with time. This factor has to be minimum for the application of ferrite in inductors which require high stability of \(\mu\) with temperature and time. In Mn-Zn ferrite Mn\(^{3+}\), Fe\(^{2+}\) pairs are formed due to the electron exchange (Fe\(^{3+} + \) Mn\(^{2+} \rightarrow Fe^{2+} + \) Mn\(^{3+}\)) between Fe\(^{3+}\) and Mn\(^{2+}\) which constitute an anisotropic configuration and diffuse gradually with time. The relaxation time of the induced anisotropy due to diffusion depends on cation vacancies and the inhomogeneity of the oxygen balance. Disaccommodation is therefore liable to occur more in iron-excess ferrite than for an iron-deficient one. However, it was also noticed\(^ {16a}\) that for Mn–Zn ferrites with iron-excess compositions fired in pure (oxygen-free) nitrogen gas, disaccommodation is not observed in the absence of cation vacancies. This implies that in addition to Fe\(^{2+}\) ions, cation vacancies have a direct effect on disaccommodation. According to Yanase\(^ {16a}\), the induced anisotropy which is associated with disaccommodation arises from cation vacancies and the presence of Fe\(^{2+}\) ions is necessary to allow the vacancies to migrate through the lattice. In other words, 'Fe\(^{2+}\)-vacancy' pairs cause the disaccommodation in Mn–Zn ferrites since the vacan-
Fig. 6—Schematic flow chart for the synthesis of Mn–Zn ferrite by (a) ceramic method and (b) coprecipitation method.

Ceramic method

(a) Ceramic method
- Raw materials (Oxides/Carbonates/Oxalates)
- Wet Mixing (Water/alcohol)
- Drying
- Calcining
- Grinding/Ball-milling
- Binder addition & Granulation
- Pressing
- Sintering
- Measurement of mag. props.

(b) Coprecipitation method
- Solution of starting materials (Chlorides/Nitrates)
- Addition to solution of precipitating agent (alkali)
- Precipitate
- Washing
- Drying

Fig. 6—Schematic flow chart for the synthesis of Mn–Zn ferrite by (a) ceramic method and (b) coprecipitation method.

cies permit diffusion of Fe$^{2+}$ ions to their energetically favourable sites. The effect can be minimised in stoichiometric ferrites and by a proper homogenization of the oxygen balance. D.F. is calculated as,

$$DF = \frac{\mu_1 - \mu_2}{\mu_1 \log t_2/t_1}$$

where $\mu_1$ and $\mu_2$ are the permeabilities measured at $t_1$ and $t_2$ minutes after demagnetization.

Synthesis of Mn–Zn Ferrite

Ceramic method

Mn–Zn ferrite powders are traditionally prepared by the ceramic method$^{17}$. The method is successful for large scale preparation of bulk ferrite powders because of its low cost and easy adaptability. However, the process has several limitations due to some inherent drawbacks such as long heating cycles at high temperatures, ball-milling of the powders for a few days to get the required particle size etc. High temperature results in sintering of powders and increasing its particle size than the optimum for a given ferrite. Ball-milling leads to a broad distribution of shape and size of particles with a poor control on morphology and microscopic homogeneity. In addition, the stoichiometry of the ferrite powder is disturbed due to the grinding of the material in steel ball-mills as it introduces variable amounts of iron as impurity.

A flow chart depicts the various steps of ferrite processing by ceramic process (Fig. 6). High purity starting materials namely oxides, carbonates, oxalates of the metal ions (iron, manganese & zinc in case of Mn–Zn ferrite) are weighed and mixed in the required proportions by wet-milling using a suitable medium like water or alcohol in a stainless steel ball-mill. After milling, the mixture is dried and calcined in inert atmosphere of nitrogen ($N_2$) at temperatures ranging from 900 to 1300°C when the formation of Mn–Zn ferrite takes place. The next step is the grinding of calcined ferrite material by ball-milling to achieve better homogenization of the product with reduced particle size to achieve the desired powder morphology and sinterability. It is one of the important processing steps of the ceramic method which controls particle size and size distribution of the resulting fine powders. Somasundaram$^{18}$ has reviewed concepts in grinding and discussed the grinding of ceramics by different methods used at present in the industrial units.

Compaction—The micron size powders are granulated by adding binders such as PVA, alginates, waxes like gum arabic, halowax etc. to get the free-flowing nature of ferrite powders required to compact into the desired shapes. This is done either by conventional compaction in a die-punch assembly by hydrostatic or isostatic compaction of the powder. A lubricant such as stearic or oleic acid is used for the die walls to avoid friction between the ferrite powder particles and with die walls also. The die-punch compacting method of pressing is commonly used in a laboratory as well as in ferrite manufacturing units with automatic presses. Johnson and Ghate$^{19}$ have described compaction of spray-dried ferrite powders using various binders and their effect on magnetic properties of the resulting compacts.

Sintering—Sintering of Mn–Zn ferrites is an important and elaborate step in its processing for the following reasons:

1. Zinc loss poses a problem when high sintered density is required.
2. Oxidation of Mn$^{2+}$ to higher valency states (and consequent reduction of Fe$^{3+}$ to lower valence state) during sintering.
3. Stabilization of Fe$^{2+}$ content consistent with the composition is necessary. It is therefore carried out under a typical firing programme$^{20}$ (Fig. 7). Some critical requirements essential for sintering of Mn–Zn ferrites$^{21}$ are given below:

1. Very high sintering temperatures are avoided to minimize zinc loss.
2. Firing temperatures are adjusted and maintained very closely during sintering.
3. For maintaining the stoichiometry and to establish the correct Fe$^{2+}$ content, carefully controlled heating and cooling rates are effected maintaining the inert gas atmosphere with varying oxygen contents to adjust equilibrium oxygen partial pressure at the corresponding temperatures.
4. An inert gas atmosphere of pure N$_2$ gas (oxygen-free) is absolutely necessary to avoid the reoxidation of Mn$^{2+}$ and Fe$^{2+}$ during cooling cycle from 1100°C down to RT. This avoids microcracks in the sintered compacts and also maintains the ratio of Fe$^{2+}$/Fe$^{3+}$ in the ferrite.

Mn–Zn ferrites, sintered with these precautions, result in the desired composition and microstructure leading to high performance material for a particular application. Nomura$^{20}$ has prepared Mn–Zn ferrites with low loss characteristics by doping with TiO$_2$ and SnO$_2$ for power supply applications at 100 kHz and 1 MHz frequencies (Table 3).

**Isostatic pressing**—It is based on the principle that pressure and heat causes densification of ceramics at much lower temperatures. Ferrite powders are isostatically pressed to get compacts with uniform density due to the uniform pressure applied in all directions on surfaces of the compact$^{21}$. In cold isostatic pressing the hydraulic pressure of the order of 10,000 to 30,000 psi is transmitted through a liquid medium such as glycerine, water or hydraulic oil against a rubber or plastic bag containing the ferrite powder. The technique has the following advantages. It gives more uniform and high density compacts. It eliminates differential shrinkage, avoids pressure cracks and is useful for pressing complex shapes.

Hot isostating pressing (HIP) is used to produce dense ceramics for critical applications such as recording heads or high power microwave ferrites. Hot pressing is the only means of achieving a dense ferrite compact at a pressure of 15,000 psi and low temperatures of 200-300°C without grain-growth. This makes it more appropriate for ferrites with a volatile component. High performance Mn–Zn ferrites with $\mu_r > 3000$ and porosity < 0.1% have been prepared using uniaxial HIP$^{22}$.

**Wet chemical methods**

In the last two decades, there has been a greater interest in the synthesis of fine powders of ceramics by using newer methods$^{23-27}$ of ultrastructure processing. These methods have resulted in tailor-making of materials having desired morphology, microscopic homogeneity, texture, chemical purity etc. Some of the important wet chemical routes are: (i) spray roasting, (ii) freeze-drying, (iii) hydrothermal oxidation, (iv) sol-gel/sol-precipitation, (v) combustion method and (vi) co-

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency for use</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_r$</td>
<td>100 kHz</td>
<td>2480</td>
<td>1473</td>
</tr>
<tr>
<td>$B_{sat} (mT)$</td>
<td>1 MHz</td>
<td>514</td>
<td>448</td>
</tr>
<tr>
<td>$\beta (mT)$</td>
<td>1 MHz</td>
<td>61</td>
<td>84</td>
</tr>
<tr>
<td>$H_c (A/m)$</td>
<td>1 MHz</td>
<td>8.2</td>
<td>10.9</td>
</tr>
<tr>
<td>Power loss at 80°C (mW/cm$^2$)</td>
<td>100 kHz (1 MHz)</td>
<td>232</td>
<td>2264</td>
</tr>
</tbody>
</table>
precipitation. Without going into the experimental details of each method, we shall review only the application of these routes for the synthesis of fine powders of Mn–Zn ferrites with high permeability and low core losses. Miscibility diagram of Mn–Zn ferrite showing the lines of constant initial permeability (μ₁) at room temperature is given in Fig. 8.

Spray roasting—The method is versatile for ferrite oxide and ferrite synthesis. An aqueous solution mixture of the metal chlorides is sprayed into a large preheated reaction vessel where the metal salts are hydrolyzed followed by oxidation in the respective oxides. The hydrochloric acid is recovered and the mixed oxide is collected at the bottom of the roaster. Ruthner²⁹ used it for the preparation of ferrite grade Fe₃O₄ using waste pickle liquor (FeCl₃ solution) from steel mills. It resulted in very pure, spherically shaped, highly uniform submicron sized particles of Fe₃O₄. Ochiai and Kimura³⁰ adopted this method for the preparation of Mn–Zn ferrite powders using FeCl₃, MnCl₂ and ZnCl₂ solutions on commercial scales claiming the following advantages over other methods: (1) increased homogeneity, (2) elimination of calcining step, (3) good magnetic properties and (4) commercial viability. Wagner³¹ has described ‘spray firing’ technique for Mn–Zn ferrite preparation where a mixed slurry is sprayed into a vertical high temperature furnace held at about 1200°C. The reaction time reported is only one minute resulting in very fine, reactive ferrite powder with better sinterability. Flame spraying also produced fine ferrite powders.

Hydrothermal oxidation method—Takada and Kiyama³² pioneered this technique for the preparation of Mn–Zn ferrite using aqueous solutions of sulphates of manganese, zinc and iron mixed in the required proportion. Complex hydroxides of these metal ions were precipitated by adding NaOH solution to the solution of sulphates until the pH value of the resultant suspension was more than 10. The suspension containing complex precipitate was heated to a temperature between 60 and 90°C and air was then bubbled through it at an optimized rate for stirring and simultaneous oxidation of complex hydroxides to Mn–Zn ferrite. Thus, ferrite particles of 0.05 to 1.0 μm could be obtained by choosing suitable reaction conditions. Particles of about 0.1 μm were obtained if pH of the suspension was kept less than 9.

Hydrothermal preparation of MnₓZn₁₋ₓFe₃O₄ ultrafine particles (10–20 nm) has been reported by Komarneni³³ at 135°C by evaporative decomposition of solutions (EDS) technique giving spherical particles of ferrites. The synthesis of Mn–Zn ferrite particles with narrow particle size distribution (the average size being in the range of 0.3 to 8 μm) has been reported by Hasegawa³⁴ using hydrothermal oxidation process.

Sol-gel/sol-precipitation method—This is a very recent technique used for the preparation of magnetic ceramics. The sol-gel technique is useful for preparing dense microspheres at low sintering temperatures. The technique provides very reactive agglomerates of very fine particles. The process consists of the preparation of a sol (an aqueous colloidal suspension of the desired oxides in hydrated form) from the nitrates or other salts by controlled precipitation. The sol is converted to a gel by partial dehydration. Sometimes the dehydration is achieved by evaporation or by dispersion of the sol as droplets in a column containing a long chain alcohol and a surfactant. The gel is completely dried and fired to a dense ceramic.³⁶,³⁷ Recently, ultrafine Mn–Zn ferrites have been prepared by amorphous citrate gel process with low loss and high permeability compositions by Ochiai and Kimura.³⁸ (Table 4a). The table compares the performance parameters of Mn–Zn ferrites prepared by citrate gel process and usual ceramic process as reported by the authors. It is very clear that loss factor is drastically reduced by gel processing. Saimanthip and Amarakoon⁵⁹ made use of sol-gel technique to achieve a uniform coating of CaO–SiO₂ film on Mn–Zn fer-

<table>
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<tr>
<th>Table 4(a)—Comparison of the performance parameters of Mn–Zn ferrites prepared by citrate gel and ceramic method²⁸</th>
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<tbody>
<tr>
<td>Process</td>
</tr>
<tr>
<td>1. Density (g/cm³)</td>
</tr>
<tr>
<td>2. μ</td>
</tr>
<tr>
<td>3. tan δ/μ (× 10⁻⁴)</td>
</tr>
<tr>
<td>4. Bₘ (G)</td>
</tr>
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</table>

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<tr>
<th>Table 4(b)—The variation of the permeability with the firing-temperature and frequency for NiₓZn₁₋ₓFe₂O₄ prepared by combustion method⁴⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sint. temp. (°C)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>900</td>
</tr>
<tr>
<td>1100</td>
</tr>
<tr>
<td>1200</td>
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</table>
Table 5—Magnetic performance parameters of Mn–Zn ferrite prepared using ‘Stabilized MnO’56

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Composition</th>
<th>μ₁ (4 kHz)</th>
<th>LF × 10⁶ (4 kHz)</th>
<th>D (g cm⁻³)</th>
<th>T₀ (°C)</th>
<th>DF × 10⁶</th>
<th>TF × 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fe₂O₃</td>
<td>ZnO</td>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>51.75</td>
<td>20.25</td>
<td>28.0</td>
<td>2640</td>
<td>1.15</td>
<td>4.72</td>
<td>135</td>
</tr>
<tr>
<td>2.</td>
<td>54.71</td>
<td>23.13</td>
<td>25.26</td>
<td>2800</td>
<td>1.72</td>
<td>4.72</td>
<td>125</td>
</tr>
<tr>
<td>3.</td>
<td>52.00</td>
<td>19.25</td>
<td>28.75</td>
<td>2720</td>
<td>1.53</td>
<td>4.77</td>
<td>150</td>
</tr>
<tr>
<td>4.</td>
<td>53.06</td>
<td>17.80</td>
<td>29.14</td>
<td>2730</td>
<td>2.70</td>
<td>4.82</td>
<td>160</td>
</tr>
<tr>
<td>5.</td>
<td>3H, Philips</td>
<td></td>
<td></td>
<td>2300 ± 20%</td>
<td>&lt;1</td>
<td>4.7-4.9</td>
<td>&gt;130</td>
</tr>
</tbody>
</table>

Table 6—Comparative evaluation of conventional, coprecipitation and spray roasting processes56

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Conventional process</th>
<th>Coprecipitation process</th>
<th>Spray roasting process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Breakdown</td>
<td>Standard</td>
<td>More</td>
<td>Less</td>
</tr>
<tr>
<td>Processing steps</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcination</td>
<td>Necessary</td>
<td>Unnecessary</td>
</tr>
<tr>
<td></td>
<td>Commination</td>
<td>Long time</td>
<td>Short time</td>
</tr>
<tr>
<td></td>
<td>Cost performance</td>
<td>Good</td>
<td>Not good</td>
</tr>
<tr>
<td>Powder properties</td>
<td></td>
<td>Primary particle size</td>
<td>0.8-3.0 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05-5 µm</td>
<td>0.4-1.0 µm</td>
</tr>
<tr>
<td></td>
<td>Size distribution</td>
<td>Wide</td>
<td>Narrow</td>
</tr>
<tr>
<td></td>
<td>Homogeneity</td>
<td>Not good</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>Purity</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Core properties</td>
<td>Good</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

droplets are sprayed into a bath of immiscible liquid such as hexane, chilled by dry ice-acetone or directly into liquid N₂, where they are subjected to the rapid freezing. The rapid freezing minimizes ice-salt segregation. The hexane has a better thermal contact with the droplets as compared to gaseous layer of nitrogen around the droplets in liquid N₂, which impedes the heat transfer. The frozen product is collected from the top of the refrigerator and is dried in vacuum at about −70°C by sublimation of ice. The freeze-drying technique gives spherical aggregated crystallites having a very low bulk density. The crystallite size can be varied by changing the calcination temperature or the concentration of the solutions to start with.

Combustion methods—(a) Solution combustion methods include those preparation techniques in which solutions are actually burned to form solid particles. A self propagating combustion method for the synthesis of spinel ferrites using metal nitrate (oxidizer) and oxalic acid dihydrizide (ODH) as fuel is reported. Ferrite is formed at ≈ 350°C almost instantaneously in less than 3 minutes. The mechanism of combustion method can be explained in terms of solution pyrolysis utilizing oxygen from metal nitrates. The exothermic reaction proceeds with the evolution of large amounts of CO₂, N₂ and water vapour. The reaction, once initiated, is catalyzed by the ferrite formed till the reaction is completed. Preparation of different compositions of NiₓZn₁₋ₓFe₂O₄ (x = 0.2 to 0.8) having large surface area (85-95 m²/g) and narrow particle size distribution has been reported. Maximum saturation magnetization of 73.4 emu/g is obtained for x = 0.5 composition. However, other magnetic performance parameters such as permeability, loss factor, T.F., DF, etc., have not been measured for these materials. The method is...
used for other spinels\textsuperscript{44} and hexagonal\textsuperscript{45} ferrites also.

(b) Combustion of solid solution precursors include combustion of precursors of the type $(\text{N}_2\text{H}_5)_x\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2(\text{N}_2\text{H}_5\text{COO})_y\text{H}_2\text{O} \ (0 \leq x \leq 1)$. Hydrazinium metal hydrazine carboxylate, at 250°C in oxygen atmosphere has been used for the preparation of Ni–Zn ferrite powders\textsuperscript{46}. The speciality of the technique is that the complex is decomposed exothermally in a single step between 120 and 200°C resulting in fine particles of the ferrite. High densities (99% of the theoretical) have been achieved with these fine materials when heated at 1100°C for 24 h as also the increased saturation magnetization of 70 emu/g. The variation of permeability with the firing temperature and frequency for a typical Ni–Zn ferrite composition is given in Table 4(b).

**Coprecipitation method**—The chemical coprecipitation of a suitable precursor such as hydroxide, carbonate or oxalate of the metal ions of interest is carried out using solutions of sulphates, chlorides or nitrates and a suitable precipitating agent such as sodium hydroxide, ammonium hydroxide, sodium carbonate or ammonium oxalate under optimized processing conditions. The processing conditions include:

(i) ratio of cations; (ii) concentration of solutions; (iii) alkali proportion; (iv) rate of precipitation; (v) temperature of precipitation; (vi) pH of slurry; (vii) method of washing ppt; (viii) pH of wash; (ix) drying temperature of the ppt; and (x) calcination temperature/time.

The precursor on ignition/decomposition yields the ferrite powder of different morphologies depending on the nature of the precursor and the processing parameters used for a given ferrite. The flow sheet in Fig. 6 explains the method in brief. Bo and Ley\textsuperscript{47} used this method to prepare low loss high stability Mn–Zn ferrites by preparing complex oxalates of manganese, zinc and iron. Precipitation of the complex oxalates was carried out at 60–70°C using 1-2M solution of sulphates and 1.2-1.6M ammonium oxalate solution as a precipitating agent. Deionized water was used for washing the precipitate free from sulphate ions, followed by drying at $\sim 180°C$ and calcining around 800°C to get the ferrite. The performance parameters reported are given below:

1. \( \mu_i = 1800 \)
2. \( \tan \delta = 1 \times 10^{-6} \) (at 100 KHz)
3. \( \text{DF} = 5 \times 10^{-6} \)
4. \( \text{TF} = 1 \times 10^{-6} \) ($-10$ to $+55\degree C$)

Other prominent contributions are from Akashi\textsuperscript{48} who reported synthesis of low loss high stability Mn–Zn ferrite using coprecipitation route and also Goldman et al.\textsuperscript{49,50} who obtained monodispersed particles of this ferrite by controlling the agglomeration of fine particles. Recently, collooidally precipitated Mn–Zn ferrites are reported by Petrovich et al.\textsuperscript{51}
In our laboratory, we have carried out coprecipitation of Mn-oxalate with small quantities of Zn oxalate to prepare solid solution of oxides of manganese and zinc, $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ ($x = 0.001-0.1$). This is a stable variety of MnO which does not absorb oxygen from ambient even on heating to a temperature of $200^\circ\text{C}$ in air and therefore referred to as 'stabilized MnO'. It was studied in detail for its optical, electrical, thermal and magnetic properties and also used for the preparation of high permeability Mn-Zn ferrite with low loss factor in the frequency range of 4 to 100 kHz. The magnetic performance parameters obtained are given in Table 5. They were reproducible for batch to batch preparations of the ferrite compositions and were also comparable with the reported data on professional grade high permeability, low loss Mn-Zn ferrites. The above discussion clearly brings out the correlation between processing and the performance of Mn-Zn ferrites. Each method described above is important in its own right though one has to adopt a suitable method keeping in view the ferrite application (Table 6).

**High frequency Mn-Zn ferrites**

In processing of high frequency Mn-Zn ferrites, minimization of the eddy current losses is a very important factor. Eddy current loss is brought about by high electrical resistivities of the ferrites. Amongst the soft ferrites, Mn-Zn ferrites have the desirable magnetic properties which make them suitable for applications in MHz range of frequencies. These properties are high saturation magnetization, high permeability and low losses up to a frequency of about 2 MHz (Table 7). These characteristics properties can be achieved by selecting some suitable compositions with the help of the composition diagram (Fig. 9). While choosing a composition care should be taken to ensure that crystalline anisotropy and magnetostriction are minimum. The phase diagram also depicts the regions where the desirable magnetic properties can be obtained. The stoichiometric composition of Mn-Zn ferrite is represented by $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$; and the optimum composition range for power ferrite as given by Ochiai is 52.5-54.5 mol % $\text{Fe}_2\text{O}_3$ and 9.0 to 14.0 mol % $\text{ZnO}$, the balance being MnO. This range of MnO and ZnO concentrations has been expanded to include a little higher MnO and ZnO concentrations in recent developments resulting in the change in position of secondary maximum of permeability (SMP) to the desired temperature range of application (such as transformer operating temperature range).

Another important factor in achieving the required characteristics of power ferrites is the microstructure. The desired microstructure for a high frequency Mn-Zn ferrite core material is a fine, uniform microstructure with grain size $>5\,\mu\text{m}$ having high grain boundary resistance. The grain size is important since the permeability of the ferrite is drastically decreased below the critical size as shown in Fig. 10 (ref. 60). Guillard related the inflection of the curve at $5\,\mu\text{m}$ to a change from domain rotation to wall-movement above $5\,\mu\text{m}$. However, many other researchers have confirmed the linear dependence of grain size upon permeabilities of 40,000 and grain size to 40 $\mu\text{m}$. An important and necessary precaution was to limit included porosity since the permeabilities drop because of intragranular porosity. It is evidenced from the fact that if pores are suppressed or located at the grain boundaries, the permeabilities increased with grain size. Apparently, for high frequency ferrites a compromise has to be made between the large grain, dense ferrites for high permeability at low frequencies and the small grain, porous ferrites for low losses at high fre-
These new methods produce powders of high purity with narrow size distribution and better sinterability, as quoted by Goldman while describing high frequency materials.

Conclusion
To summarize, we arrive at the following conclusions regarding the processing of this professionally important ferrite:
Conventional ceramic methods have been improved through the use of active raw materials and dopants. The new methods of processing developed over the last two decades have turned out to be fruitful in this regard.
Processing of Mn–Zn ferrites by wet-chemical methods has proved to be advantageous with respect to the quality of ferrite powders as compared to the conventional method of processing. These new methods produce powders of high purity, better homogeneity and fine particle size with narrow size distribution and better sinterability.

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