

Chapter-2  
Preparation Techniques

## 2.1 Preparation Technique

Synthesis of nanograin size particles proves to be one of the most interesting and important technique in the field of material science, as the small grain size particles have some of the interesting properties when compared to bulk particles in material processing and technological applications. These particles have improved magnetic, dielectric, catalytic properties, as they possess high resistivity and negligible eddy current losses [1-5]. The preparation technique plays important role in surface properties and Curie temperature ( $T_c$ ) can be varied by substitution of non-magnetic cations. Nano- magnetic particles exhibit some interesting properties such as high frequency devices, magnetic fluids, high density recording, colour imaging etc [6-8].

The various processing techniques, which are used for the synthesis of spinel ferrite powders include, microwave refluxing [9], sol-gel [10-13], hydrothermal [14, 15], co-precipitation [16], spray pyrolysis [17]. In fact there are numerous papers on synthesis of nickel ferrite by various methods. In our present investigation we employed sol-gel auto-ignition method to synthesize ferrite powders. The sol-gel auto-ignition method is used to speed up the synthesis of complex materials. It is a simple process, a significant saving in time and energy consumption over the traditional methods, and requires less sintering temperature. This method is employed to obtain improved powder characteristics, more homogeneity and have a narrow particle size, thereby influencing structural, electrical, and magnetic properties of spinel ferrites. Small crystalline size of the resultants may have an important influence on the particles of the materials prepared.

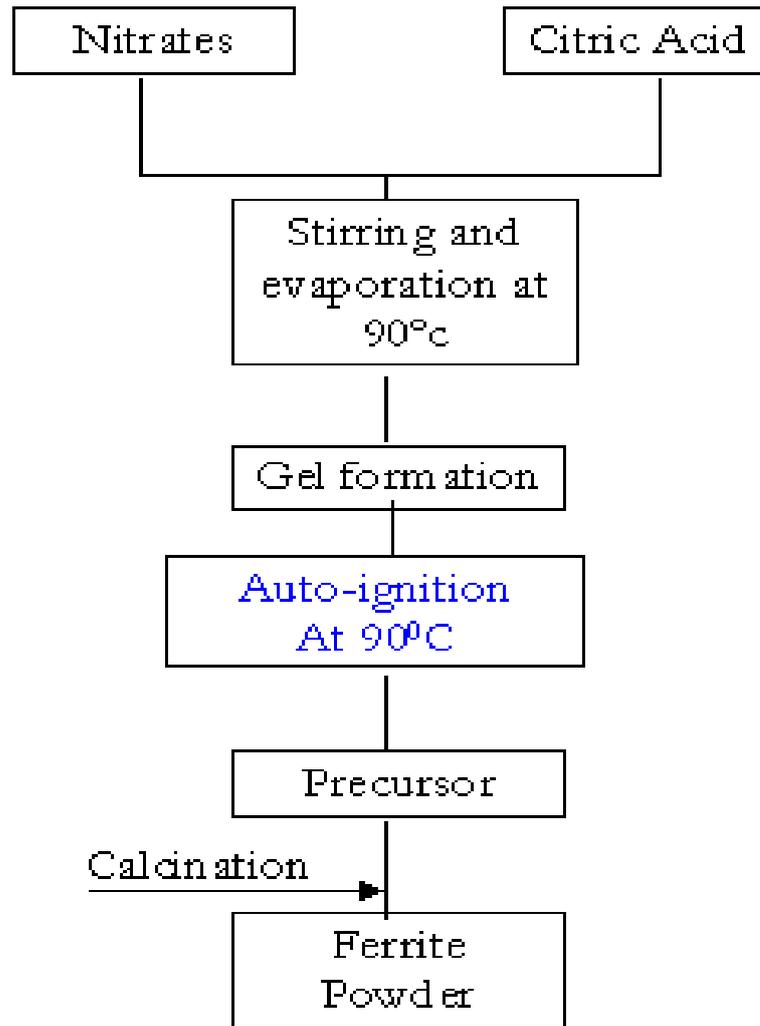
Sol-gel synthesis includes three different techniques namely, (a) auto-ignition, (b) auto-combustion, (c) Pechini synthesis.

The detailed description of the synthesis process of the three methods is described as follows:

### **2.1 (a) Sol-gel auto-ignition Method**

In this method the initial compounds were taken in the form of nitrates, as they dissolve easily in water, and if the initial solution mixture is in liquid form one can get very homogeneous powders. The flowchart is given in Figure 2.1. The Figure shows the detailed process in obtaining the required ferrite powders by sol-gel auto-ignition method [18].

The nitrates were used as starting materials and citric acid as chelating material. The molar ratio of metal nitrates to citric acid has been taken in molar ratios. The metal nitrates were dissolved together in a minimum amount of de-ionized water to get a clear solution. An aqueous solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the PH at 7. After thorough mixing of the chemical solution one has to ensure that the solution is free from any unwanted substance. The mixed solution was moved on to a hot plate with continuous stirring at 90<sup>0</sup>C. During evaporation, the solution became viscous and finally formed a very viscous brown gel. When finally all remaining water was released from the mixture, the sticky mass began to bubble. After several minutes the gel automatically ignited and burnt with glowing flints. The decomposition reaction would not stop before the whole citrate complex was consumed. The auto ignition was completed within a minute, yielding the brown colored ashes termed as a precursor. The final calcinations temperature has been decided from the thermal analysis, as described in the results and discussions chapter 4, 5 and 6. From our present study we have calcined the powders at 500<sup>0</sup>C, for nearly four hours to study the structural and magnetic properties.



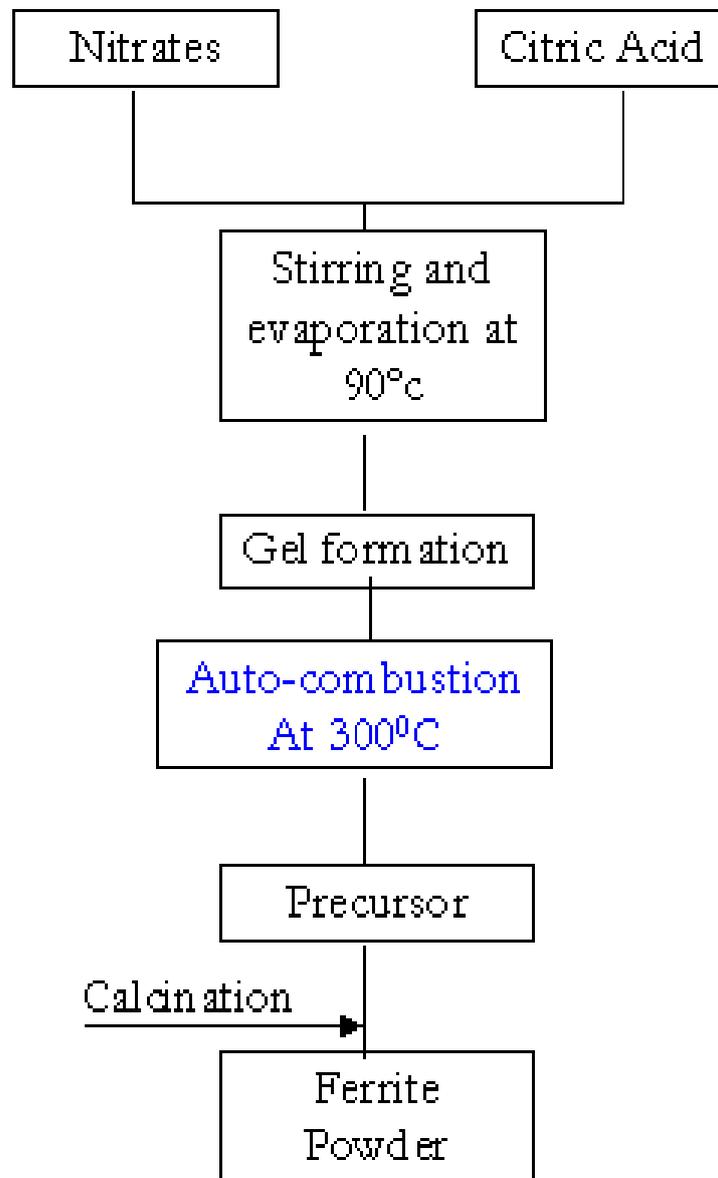
**Figure 2.1: Flowchart for the preparation of Ferrite powders by Sol-gel auto-ignition**

**Note:** In the present chapter we have explained the different methods in sol-gel technique, as before choosing the auto-ignition method we have tried with all these methods. As we found the sol-gel auto-ignition method to be simple and economic way for obtaining the ferrite powders, all our discussion on the structural, thermal and magnetic properties are confined to this method only.

## **2.1 (b) Sol-gel auto-combustion Method**

This method is similar to the method as described above till the gel formation. Once the gel is formed the beaker with gel is moved on to the mantle and the temperature is increased to 300<sup>0</sup>C (Fig2.2). As the temperature of the beaker reaches high the entire gel is transformed into glowing flints and the entire process would not stop till the citric acid is not consumed [19]. The obtained precursor powders will also show some interesting properties, but the structural changes, which are taking place at low temperature i.e. the initial phase of the compound formation, cannot be investigated. This is because they obtained powders by this method are pre-sintered at 300<sup>0</sup>C.

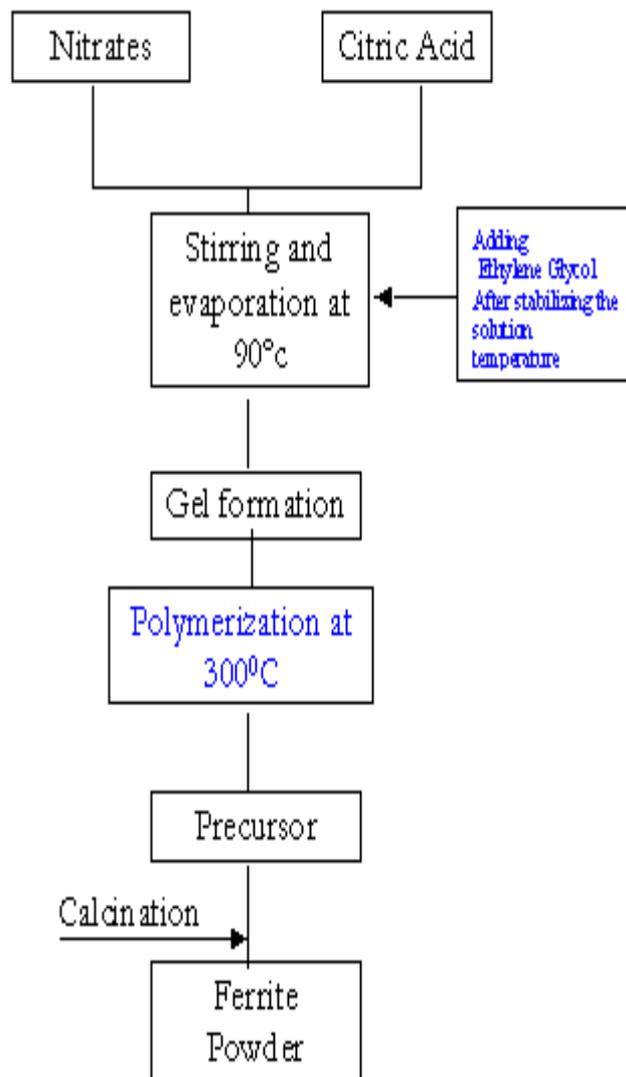
**Note:** This is from our experimental observation, and as we have employed sol-gel auto-ignition method, our results, data are confined to sol-gel auto-ignition method only.



**Figure 2.2: Flowchart for the preparation of Ferrite powders by Sol-gel auto-combustion**

## 2.1 (c) Pechini Method

This is also one of the sol-gel techniques employed by Pechini [20-23]. The metal nitrate mixture was heated to 90 °C, at which point ethylene glycol was added at a mass ratio of 40:60 with respect to citric acid (Fig2.3). The temperature was maintained constant up to gel formation, which polymerized at 300 °C.



**Figure 2.3: Flowchart for the Ferrite powders by Pechini method**

## 2.2 Magnetic Properties

**Bohr magneton**  $\eta_B \quad \mu_B$ : The magnetic moment of the electron is called as Bohr magneton.

**Coercivity ( $H_c$ ):** In the applied field is reversed, by reversing the current I the magnetization winding, the induction will decrease to zero when the negative applied fields are equals is called coercivity  $H_c$ , it is measured in Oersted (Oe). Coercivity is used to differentiate between soft and hard spinel ferrites.

**Remanent magnetization ( $M_r$ ):** If the magnetic field is reduced to zero after saturation has been reached in the positive direction, the induction will decreases from saturation region ( $M_s$ ) to  $M_r$  known as remanent or residual magnetization, it is measured in emu/g.

**Saturation magnetization ( $M_s$ ):** The maximum position reached with the maximum applied magnetic field is called as saturation magnetization ( $M_s$ ), it is measured in emu/g.

**Permeability ( $\mu$ ):** is the degree of magnetization of a material that responds linearly to an applied magnetic field. Magnetic permeability is represented by the Greek letter  $\mu$ .

### 2.3 Neel's theory of Ferrimagnetism

1. Neel's theory of ferrimagnetism has been successfully used to explain magnetic properties of the spinel ferrites. Neel's theory [24] is based on the following assumptions.
2. A ferrimagnetic crystal lattice could be divided into two sublattices, tetrahedral (A) and octahedral [B] sites. The magnetic ions are assumed to be distributed among the tetrahedral (A) sites and the octahedral [B] sites of the spinel structure. Negative (antiferromagnetic) exchange interaction exists between A and A, A and B, and B and B.
3. There exists one type of magnetic ions in the material, of which a fraction  $\lambda$  appear on A sites and a fraction  $\mu$  appears on B sites. Thus,

$$\lambda + \mu = 1 \quad (2.1)$$

4. The A-B and B-A interaction are identical and predominate over A-A and B-B interaction and therefore the net magnetic moment is the difference between the two average sublattice magnetic moments.
5. An internal Weiss molecular fields acts on the ions. For a simple ferrite of the form  $MFe_2O_4$ , which satisfies Neel's assumptions, the magnetic ions are trivalent ferric  $Fe^{3+}$ , M is non-magnetic ion, the cation distribution formula can be written as



(since  $\mu = 1 - \lambda$  )

Where the bracketed ions are those on the octahedral sites.

Neel defines the interaction within the material from Weiss molecular field view point.

The magnetic field acting upon an ion is written as

$$H = H_o + H_m \quad (2.4)$$

Where  $H_o$  is external applied field and  $H_m$  is the internal or molecular field.

Applying the molecular field concept to a ferrimagnetic material we have

$$H_A = H_{AA} + H_{AB} \quad (2.5)$$

$$H_B = H_{BB} + H_{BA} \quad (2.6)$$

Where  $H_A$  - represents the molecular field acting on an ion on A site

$H_{AA}$  - is the molecular field due to neighbour A ions and

$H_{BB}$  - is the molecular field due to its neighbour on B sites.

The molecular field component may be written as

$$H_{AA} = \gamma_{AA} M_A, H_{AB} = \gamma_{AB} M_B \quad (2.7)$$

$$H_{BB} = \gamma_{BB} M_B, H_{BA} = \gamma_{BA} M_A \quad (2.8)$$

Where the  $\gamma$ 's are the appropriate molecular field coefficients and  $M_A$  and  $M_B$  are the magnetic moments of the A and B sublattices. It may be shown that,  $\gamma_{AB} = \gamma_{BA}$ , but

$\gamma_{AB} \neq \gamma_{BA}$ , unless the two sublattice are identical.

The total magnetic field in the external applied  $H_o$  acting on each sub lattice may be given as:

$$H_A = H_o + \gamma_{AA} M_A + \gamma_{AB} M_B \quad (2.9)$$

$$H_B = H_o + \gamma_{BB} M_B + \gamma_{BA} M_A \quad (2.10)$$

## 2.4 Yafet Kittel Theory of Ferrimagnetism

The Neel's theory of ferrimagnetism fails to explain the deviation observed between the variation of Neel's magnetic moment and observed saturation magnetic moment. So the models like Yafet Kittel [25], Gilleo [26, 27] were proposed to explain this anomaly. It was shown by Yafet and Kittel that in spinel ferrites, a non-collinear or canted spin arrangement occur on substitution of non-magnetic cation in one sublattice. As a result, the B sublattice splits into two, i.e. B1 and B2 with equal magnetic moments at angle  $\theta$  so called Yafet angle  $\theta_{YK}$  with the direction of net magnetization of B sublattice at 0K.

The mixed ferrites  $Zn_xNi_{1-x}Fe_2O_4$  or  $Fe_2O_3$ , provides experimental evidence supporting the Y-K model. Pure Ni ferrite ( $x=0$ ) has the inverse spinel structure, and the B-B interaction is dominated. Pure Zn ferrite has the normal spinel structure;  $Zn^{2+}$  being non-magnetic, the A site carry no magnetic moment. The B-B interaction is expected to give rise to antiferromagnetic ordering in the B lattice. As x is varied from 0 to 1, intermediate arrangement will arise.

At a particular value of (x), the A-A interaction and B-B interaction are comparable. The B-B interaction arranges magnetic moments on B lattice in anti-parallel direction whereas A-B interaction arranges them in parallel direction on B site. This leads to a canted spin arrangement on B-site. The Yafet-Kittel model splits B sub-lattice into  $B_1$  and  $B_2$  sub-lattices each making an angle  $\theta_{yk}$  with the direction of net magnetization of B sub-lattices. The moment on B site is anti-parallel to moment on A site. The net magnetic moment for the system can be expressed as

$$\mu_x = M_B \cos\theta_{YK} @ M_A \quad (2.11)$$

Where,  $M_A$  is magnetic moment on A site and  $M_B$  is magnetic moment on B site.

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