CHAPTER II
Synthesis and Characterization of Nd$^{3+}$ Substituted Mg-Cd Nanocrystalline Ferrites
2.1 Synthesis of Nd$^{3+}$ Substituted Mg-Cd Nanocrystalline Ferrites

2.1.1 Introduction

Ferrite is a ferrimagnetic material, brown or black in color and having general chemical formula MFe$_2$O$_4$, where M is divalent metal ions and Fe is trivalent iron ion. The synthesis process of ferrite goes through various steps. According to Standley [1], ferrite materials are synthesized under the following important steps.
1. Mixing chemicals in stoichiometric proportion.
2. Presintering of mixed chemicals.
3. Milled to have fine powder and pressed into required shape.
4. Sintering carried out to form final product.

2.1.2 Methods of Ferrite Synthesis

Standley [1] describes four methods for preparation of ferrites,
1. The oxide method
2. Decomposition method
3. Hydroxide method
4. Oxalate method

1. The oxide method

It is easiest to use with little chemical knowledge. The required proportions of high purity oxides metal for final product are mixed together. They are mixed manually or wet milled with steel balls for few hours. After milling the mixture is dried and passed through the mesh screen. The mixture is calcinated at elevated temperature, powdered and dried. It is then pressed to suitable shape and subjected to final sintering.

2. Decomposition method

In this method salts such as carbonates, nitrates and oxalates instead of oxides are used as starting materials. These are mixed in requisite proportion and preheated, usually in air to produce oxides by thermal decomposition. Other details of this method are similar to the oxide method.

3. Hydroxide precipitation

The lengthy milling process in dry mixing can be avoided by using this method. In this method attempts have been made to precipitate simultaneously the required hydroxides from solution. The precipitate contains required metal ions in desired proportion and intimately mixed. In order to determine the pH value of complete

4. Oxalate Precipitation

Ammonium oxalate was used to obtain precipitation of metallic oxalates, which does not leave any residue after heating. Also most metal oxalates have crystal structure. Thus, the precipitation creates mixed crystals of the metallic cations with right proportion with which they presents in solution. The advantage of this method is mixing of metal ions on molecular scale, which results greater reactivity and homogeneous product. This method gives ferrites having nanoparticle size.

2.1.3 Presintering, Milling and Final Sintering

The purpose of presintering is to decompose carbonates, oxalates and higher oxides. It assists homogenization of material and reduces the shrinkage during final sintering. The presintered powder is re-milled in an organic medium such as alcohol or acetone and mixed with binder such as polyvinyl acetate. The dried powder is introduced into suitable shaped die and subjected to high pressure using hydraulic press. The compressed material of desired shape is subjected to final sintering at which the solid state reaction occurs.

2.1.4 Mechanism of Solid State Reaction

In order to get a reliable final product, it is necessary to take into account the phase equilibrium of the system during final sintering. During the formation of ferrites the solid state reaction may be regarded as diffusion of divalent metal oxide MO and iron oxide Fe$_2$O$_3$. At the beginning, there is only one phase boundary between these two reactants. Once the nucleation of ferrite MFe$_2$O$_4$ occurs, there appear two more phase boundaries, viz. (a) between MO and the ferrite MFe$_2$O$_4$ and (b) between Fe$_2$O$_3$ and MFe$_2$O$_4$ shown in the Fig 2.1. Further progress of reaction can only take place by transport of reactants through the ferrite phase. There are three possible mechanisms [3].

1. The counter diffusion in which the oxygen ions remain essentially stationary and only cations migrate in opposite directions.

2. Even anions can migrate, and the diffusion of cations is compensated by an associated flux of anions $O^{2-}$ instead of counter-current of another cation.

3. Iron in reduced state Fe$^{2+}$ may diffuse through the ferrite layer. During such a process oxygen in gaseous phase is transported; it is given off at MFe$_2$O$_4$/Fe$_2$O$_3$ interface and taken up at MO/MFe$_2$O$_4$ boundary.
The ferrite materials are generally synthesized by standard ceramic method. But this method has several disadvantages like inhomogeneity of product, requirement of higher sintering temperature and time. It also consumes costly chemicals in form of oxides. The chemical methods such as co-precipitation [4], combustion [5], hydrothermal
sol-gel [7], citrate precursor [8] and thermal decomposition [9] etc overcome these disadvantages. The chemical methods yield homogeneity at molecular scale. On literature survey, it is found that, among all chemical methods, co-precipitation method is an effective, superior and requires low cost chemicals for the preparation of nanocrystalline ferrites. This method requires low sintering temperature, achieves excellent control of crystallite size [10], improves homogeneity and yields high purity and fine powder [11].

Several researchers employed the conventional sintering technique for the preparation of ferrites [4, 10-12]. The structural properties of magnesium substituted ferrites prepared with conventional sintering technique were reported by number of researchers [13-16]. Gadakari et al. [13] reported the crystallite size in the range 27.79-30.40 nm and grain size 0.589-1.204 µm of Mg-Cd ferrites synthesized by oxalate co-precipitation method using final sintering temperature 1050°C for 5 h. The Mg-Cu-Zn ferrite was prepared by Zhou et al. [14] using sintering temperature of 950°C for 2 h. Vinayak et al.[15] observed the particle size of 10nm to 31nm for synthesized Co-Mg ferrite sintered at 550°C for 4 h by using sol-gel auto combustion method. Karche et al. [16] prepared Mg-Cd ferrites using ceramic method followed by conventional sintering at 1000°C for 48h. The conventional sintering technique, due to non-uniform heating in the furnace, results in absences of few ferrite phases during the formation of material. The conventional method of heating also suffers from the drawbacks like energy and time consumption.

The microwave heating is fastest technique of sintering used for synthesis of ferrite materials. This method overcomes the drawbacks of conventional sintering technique [17]. In this technique, microwaves are allowed to fall on material that may absorb, reflect or transfer through the material. When microwaves are absorbed by the material, due to phenomenon of dielectric heating, its temperature increases rapidly [18]. Due to this sudden temperature rise, the constituent metal oxalates are rapidly converted into ferrite. The uniform heat maintains individual phases of the material [19]. Ponzoni et al. [20] concluded that reaction time in conventional hydrothermal synthesis is significantly more than the microwave assisted hydrothermal synthesis. Microwave synthesis technique enhances the rate of chemical reactions and gives superior yields in some cases [21]. Cobalt ferrite nano-particles were successfully prepared by polyol method using both conventional and microwave heating techniques [22].
The characteristics of ferrites are influenced by foreign substitutions like rare earths. Luo [23] successfully prepared the nano sized Nd$^{3+}$ doped strontium ferrite by chemical co-precipitation method [23]. Gilani *et al.* [24] reported that Nd-doped lithium–cobalt nanocrystals have the possible use in high frequency device applications and high density recording media. Shinde *et al.* [25] studied structural and electrical properties of nanocrystalline Nd$^{3+}$ substituted Zn-ferrite synthesized by oxalate co-precipitation technique under conventional sintering technique. Thankachan *et al.* [26] studied effect of Nd$^{3+}$ substitution on the structural properties of magnesium ferrite prepared by the sol–gel technique and reported that occurrence of extra phases in cubic spinel ferrite for substitution of Nd$^{3+} \geq 0.25$.

However, no report is found in literature for Nd$^{3+}$ substituted Mg-Cd ferrites synthesized by oxalate co-precipitation method with microwave sintering technique. Therefore it was decided to synthesis Nd$^{3+}$ substituted Mg-Cd ferrites by oxalate co-precipitation method with microwave sintering technique and studies their structural and electromagnetic properties such as permittivity, permeability, dielectric and magnetic loss tangents. These synthesized ferrites are used as substrate in designing and fabricating microstrip patch antenna.

### 2.1.5 Experimental

#### Preparation

The nanocrystalline ferrite system with chemical formula Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 for y = 0 and 0.03) were prepared by the oxalate co-precipitation method with microwave sintering technique. The high purity AR grade magnesium sulphate (MgSO$_4$.7H$_2$O, purity 99.5%, supplied by Thomas Baker), cadmium sulphate (3CdSO$_4$.8H$_2$O, purity 98%, supplied by Thomas Baker), neodymium sulphate (Nd$_2$ (SO$_4$)$_3$.8H$_2$O, purity 98%, supplied by Thomas Baker) and ferrous sulphate (FeSO$_4$.7H$_2$O, purity 99.5%, Thomas Baker) were used as starting materials. All chemicals were weighted in desired stoichiometric proportion on single pan microbalance. They were dissolved in 1000 ml double distilled water at room temperature and subjected to continuous magnetic stirring. The concentrated H$_2$SO$_4$ was added drop by drop to maintain the pH of solution at 4.8 [27]. The solution was heated at about 80$^0$C until its volume reduced to half, for proper mixing of chemicals at molecular scale and was allowed to cool. 0.1 N solution of precipitating agent was prepared in double distilled water by dissolving di-ammonium oxalate monohydrate ((NH$_4$)$_2$
C₂O₄·H₂O, supplied by Thomas Baker). This solution was added drop by drop to cooled metal sulphate solution with continuous stirring to get complete precipitation [28]. The chemical reactions in the process of precipitation can be written as follows [1]:

\[
\text{MgSO}_4 + 2\text{H}_2\text{O} + 2\text{C}_2\text{O}_4^- \rightarrow \text{MgC}_2\text{O}_4·2\text{H}_2\text{O} + \text{SO}_4^{2-} \quad \quad \text{------- (2.1)}
\]

\[
\text{CdSO}_4 + 2\text{H}_2\text{O} + 2\text{C}_2\text{O}_4^- \rightarrow \text{CdC}_2\text{O}_4·2\text{H}_2\text{O} + \text{SO}_4^{2-} \quad \quad \text{------- (2.2)}
\]

\[
\text{NdSO}_4 + 2\text{H}_2\text{O} + 2\text{C}_2\text{O}_4^- \rightarrow \text{NdC}_2\text{O}_4·2\text{H}_2\text{O} + \text{SO}_4^{2-} \quad \quad \text{------- (2.3)}
\]

\[
\text{FeSO}_4 + 2\text{H}_2\text{O} + 2\text{C}_2\text{O}_4^- \rightarrow \text{FeC}_2\text{O}_4·2\text{H}_2\text{O} + \text{SO}_4^{2-} \quad \quad \text{------- (2.4)}
\]

The solution with bright yellow precipitate was the mixture of magnesium, cadmium, neodymium and ferrous oxalates. For digestion, precipitated solution was kept on the sand bath in order to settle down the precipitate. Thereafter the precipitate was filtrated by using Whatman filter (no.41) and vacuum pump operated suction flask. The precipitate was finally washed with distilled water to remove excess ammonium oxalate and sulphate contaminant. The total removal of sulphate ions was confirmed by using barium chloride test. The barium chloride test was carried out by using 0.1 N solution of barium chloride. It was added in the filtered solution and observed. If the white precipitate was observed in the filtered water, then it shows some sulfate ions are present in the filtered solution. Again the precipitate of metal oxalate was washed with distilled water, until the white precipitate is not observed in filtered solution. The precipitate was dried in open environment by keeping it on hot plate for time of 1hour. The dried precipitate was milled in an agate mortar by using AR grade acetone as a base. The milled powder was poured into alumina crucible and placed into a cylindrical cavity formed inside a brick. As the metal oxalates in the precipitate are poor absorbers of microwave radiation, the space between alumina crucible and wall of the cavity in the brick was filled with aluminum powder. The aluminum powder is a moderate absorber of microwave radiations [29]. It was used as microwave subsector for heating [29]. The brick with crucible was placed on the turn table of microwave oven (ONIDA 20XL, 800watt, operated at 2.45 GHz) for presintering. The oven was operated at 40% power for 10 minutes. The brick was immediately removed from the oven. The cooled presintered powders were again milled in agate mortar.

To optimize the better microwave oven power for final sintering of the ferrites under investigation, the sample powder MgₐCd₀.₆Fe₂O₄ was final sintered for 10 min at
power values of 50%, 60%, 70%, 80% and 90% [30]. Considering the results of X-Ray diffraction, other sample powders were sintered at 70% of the power for 10 min.

The sintered powder was milled to have a fine powder. For pallet formation, a 0.1N polyvinyl acetate as binder mixed in fine powder and dry powder was pressed under hydraulic press with pressure of about 5 Ton for 5 min. in a circular die of diameter 13mm. These pellets where finally sintered at 70% oven power for 10 min. The procedure of preparation of ferrite under investigation is presented in Fig.2.2.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Details of various step in the preparation ferrites</th>
<th>Figures</th>
<th>Sr. No.</th>
<th>Details of various step in the preparation ferrites</th>
<th>Figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weighting of starting chemicals in desired proportion</td>
<td><img src="image1.jpg" alt="Figure 1" /></td>
<td>2</td>
<td>Starting chemicals dissolved in double distilled, adding of concentrated H₂SO₄ and then heating for proper mixing of chemicals.</td>
<td><img src="image2.jpg" alt="Figure 2" /></td>
</tr>
<tr>
<td>3</td>
<td>Addition of precipitating agent drop by drop to cooled metal sulphate solution with continuous stirring to get complete precipitation</td>
<td><img src="image3.jpg" alt="Figure 3" /></td>
<td>4</td>
<td>For digestion, precipitated solution was kept on the sand bath in order to settle down the precipitate</td>
<td><img src="image4.jpg" alt="Figure 4" /></td>
</tr>
<tr>
<td>5</td>
<td>Filtration of precipitated solution using Whatman filter (no.41) and vacuum pump operated suction flask</td>
<td><img src="image5.jpg" alt="Figure 5" /></td>
<td>6</td>
<td>Washing of precipitate by distilled water to remove excess ammonium oxalate and sulphate contaminant.</td>
<td><img src="image6.jpg" alt="Figure 6" /></td>
</tr>
<tr>
<td>7</td>
<td>The precipitate was dried in open environment</td>
<td><img src="image7.jpg" alt="Figure 7" /></td>
<td>8</td>
<td>Milling of dried precipitate in an agate mortar by using AR grade acetone as a base</td>
<td><img src="image8.jpg" alt="Figure 8" /></td>
</tr>
<tr>
<td>9</td>
<td>The milled powder was poured in to alumina crucible and placed into a cylindrical cavity formed inside a brick</td>
<td><img src="image9.jpg" alt="Figure 9" /></td>
<td>10</td>
<td>The brick with crucible was placed on the turn table of microwave oven</td>
<td><img src="image10.jpg" alt="Figure 10" /></td>
</tr>
<tr>
<td>11</td>
<td>The oven was operated at 70% power for 10 minutes</td>
<td><img src="image11.jpg" alt="Figure 11" /></td>
<td>12</td>
<td>Immediate removal of brick from the oven kept to cool. Milling of cooled presintered powder to obtain final sample powder.</td>
<td><img src="image12.jpg" alt="Figure 12" /></td>
</tr>
</tbody>
</table>

**Fig.2.2** Photographical presentation of preparation of ferrite.
The physical density of sintered pallets was determined by using Archimedes principle using formula [31],

\[ \rho_p = \frac{w_p}{w - w_x} \]  

where, \( w \) = Weight of sample in air,
\( w_x \) = Weight of sample in xylene,
\( \rho_x \) = Density of xylene.

2. 1.6 Results and Discussion:

The samples under investigation resulting into very fine brown colored powder preliminary indicate the formation of ferrites. The physical density of pelletized samples of \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\( x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 \) for \( y = 0 \) and 0.03) system was presented in TABLE 2.3. From this table, it is seen that physical density of the ferrites with \( y = 0 \) and \( y = 0.03 \) lie in the range of 4.258-6.356 gm/cc and 4.373-6.476 gm/cc. It is observed that the physical density of Mg-Cd ferrites and Mg-Nd-Cd ferrite decreases with increase in Mg\(^{2+}\) content and is attributed to mass to volume ratio corresponding to divalent cations [32]. It is also seen that the physical density of Mg-Cd ferrites is less than that of Mg-Nd-Cd ferrite ferrites. This is due to the larger molecular weight for Mg-Nd-Cd ferrite than Mg-Cd ferrite.

Variation of physical density of Mg-Cd ferrites with Mg content in present study and that reported for Mg-Cd ferrites prepared by co-precipitation method with conventional sintering technique [13] are presented in Fig. 2.3. From this figure, it is seen that, the physical densities of ferrites prepared under investigation are higher than those for ferrites prepared by co-precipitation method with conventional sintering.

![Graph showing variation of physical density with Mg content](image)

**Fig.2.3** Variation of physical density with Mg content for \( \text{Mg}_x\text{Cd}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x = 0, 0.2, 0.4, 0.6, 0.8 \) and 1.0) system.
2.2 Characterization of ferrites

2.2.1 X-ray Diffraction Studies

2.2.1.1 Introduction

The X-ray diffraction techniques are broadly used in materials science for structural analysis. It is a most important characterization technique to study the crystal structure of materials. The primary characterizations such as phase confirmation, crystallite and unit cell size determination, recognition of the crystal structure and fundamental unit cell modeling are done by using this method [33]. X-ray powder diffraction is mainly used for the identification of unknown crystalline structures [34]. The principle of XRD is based on phenomenon of diffraction and particularly on Bragg’s law.

X-ray is electromagnetic radiation having short wavelength comparable in magnitude to the atomic spacing with high energy. The wave is diffracted when it strikes a sequence of repeatedly spaced obstacles which are able to scatter the wave and have spacing that are nearly equal to the wavelength. When X-ray beam strikes a solid material, a fraction of it gets scattered in all directions by ions or electrons which are coming in the path of beam. The essential condition for the diffraction of X-ray by a regular arrangement of atoms is presented in Fig. 2.4. It shows two parallel planes (P-P' and Q-Q') of atoms with same Miller indices (h, k, l) and are separated by interplaner spacing \( d \). When a monochromatic, coherent and parallel beam of X-ray of wavelength \( \lambda \) is incident on two planes at an angle \( \theta \), they are scattered. If the path difference between parallel planes P-P' and Q-Q' is equal to whole number \( n \) of wavelength \( \lambda \), then constructive interference occurs between scattered rays. This condition of diffraction is known as **Bragg’s law** and mathematically represented by Eq. (2.6).

\[
2d_{hkl} \sin \theta_{hkl} = n\lambda
\]  

where,

- \( d \) = the interplaner distance
- \( n \) = order of diffraction
- \( \lambda \) = the wavelength of monochromatic X-ray.

For first order (i.e. \( n = 1 \)) in the Bragg’s equations (2.7),

\[
2d_{hkl} \sin \theta_{hkl} = \lambda
\]  

\[\text{(2.7)}\]
There are three well-known methods of X-ray diffraction depends on change in glancing angle (θ) and wavelength (λ) [34].

1. **X-ray powder diffraction method**

   This method is independently created by Hull [35] and Debye and Scherer [36]. This is commonly used method to identify and determine the crystal structures and lattice parameters. The basic principle of this method depends on fixed wavelength (λ) and changeable glancing angle (θ).

2. **Laue method**

   This method is used for single crystal. The single crystal is kept steady in the path of X-ray beam. The incident X-rays of suitable wavelength chosen by the crystal and diffract at glancing angle (θ) satisfying Bragg’s law. The main theme of this method was to obtain crystal perfection and orientation of a single crystal.

3. **Rotating crystal method:**

   In the field of X-ray crystallography, this method has much importance. The principle of this method is based on mounting of crystal. The single crystal is mounted in such way that its one of the axis must be perpendicular to the X-ray beam. When crystal rotates, particular set of lattice planes makes the write glancing angle (θ) at which Bragg’s law is satisfied.

2.2.1.3 **Experimental**

The X-ray diffraction patterns of MgₙCd₁₋ₙNdₓFe₂₋ₓO₄ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 and y=0, 0.03) system were recorded on X-ray powder diffractometer model D2-Phaser with Cu-Kα (λ = 1.5406 Å) radiation. The ferrites in the form of powder were scanned in the range of 20° to 80° with step size of 0.0202° and X-ray excitation at
power 30KV and of current 10mA. The lattice constant and inter planer distances were calculated by using following relations.

\[ d_{\text{hkl}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  

\[ d_{\text{hkl}} \] - the inter-planner distance

\( hkl \) - the Miller indices

‘a’ - lattice constant.

By combining equation (3) and (4), We have

\[ (h^2 + k^2 + l^2) = \frac{4a^2 \sin^2 \theta_{\text{hkl}}}{\lambda^2} \]  

\[ (h^2 + k^2 + l^2) \] - inter-planer distance

The average crystallite size of all ferrites (D) was determined by Debye Scherrer [37] formula using (311) plane,

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

\( \lambda \) - X-ray wavelength

\( \beta \) - The full width at half maxima

\( \theta \) - Bragg’s diffraction angle

The Bond lengths \( (\text{A-O and B-O}) \) and ionic radii \( (r_A \text{ and } r_B) \) on A-site and B-site of the ferrites under investigation are calculated by using equations [1],

\[ \text{A - O} = (U - \frac{1}{4})a\sqrt{3} \]  

\[ \text{B - O} = (\frac{5}{8} - U)a \]  

\[ r_A^2 = (U - \frac{1}{4})a\sqrt{3} - r_0^2 \]  

\[ r_B^2 = (\frac{5}{6} - U)a - r_0^2 \]  

Where \( a \) - lattice constant

\( U \) - oxygen ion parameter

\( r_0^2 \) - radius of oxygen ion (1.35 Å)

For \( \text{CdFe}_2\text{O}_4 \) \( U = 0.389 \) and for \( \text{MgFe}_2\text{O}_4 \) \( U = 0.382 \) and for remaining samples intermediate values of \( U \) were used.
2.2.1.4 Results and Discussion

The X-ray diffractograms for \( \text{Mg}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4 \) powder sintered in microwave oven at operating powers of 50%, 60%, 70%, 80% and 90% for 10 min are presented in Fig. 2.5.

![Fig. 2.5 X-ray diffractograms for \( \text{Mg}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4 \) ferrite prepared at various oven powers](image)

The existence (220), (221), (311), (400), (422), (511/333) and (440) planes in the diffractograms confirms the formation of cubic spinel structure of ferrites. The intensities of prominent (311) peak, representative of ferrite phase at various operating powers and crystallite size (D) with corresponding angle of diffraction are presented in **TABLE 2.1**.

<table>
<thead>
<tr>
<th>Power % Watt</th>
<th>Diffraction Angle (2θ) Degree</th>
<th>Peak Intensity (311 plane) (Counts)</th>
<th>Crystallite size (D) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>35.36</td>
<td>781.83</td>
<td>7.7</td>
</tr>
<tr>
<td>60</td>
<td>35.36</td>
<td>860.83</td>
<td>7.88</td>
</tr>
<tr>
<td>70</td>
<td>35.16</td>
<td>891.26</td>
<td>10.90</td>
</tr>
<tr>
<td>80</td>
<td>35.16</td>
<td>794.87</td>
<td>9.08</td>
</tr>
<tr>
<td>90</td>
<td>35.16</td>
<td>735.89</td>
<td>6.51</td>
</tr>
</tbody>
</table>
From this table, it is confirmed that powder sintered at power 70% for 10 min, shows all well defined intense peaks compared to that sintered at other powers (50%, 60%, 80% and 90%) for 10 min. The average crystallite size (D) of ferrites is increases, reaches maximum value (10.9 nm) at power 70% and then decreases with increase of power. So all ferrite under investigation are sintered at 70% power of microwave for 10 min.

The X-ray diffractograms of Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 and y=0, 0.03) systems are presented in Fig.2.6 and Fig.2.7. Various planes in the diffractograms with angles (2θ) of 30.07°, 35.56°, 42.86°, 56.66°, 62.33°, 66° corresponding to (220), (311), (400), (422), (511/333) and (440) have been observed. The existence of these planes in the diffractogram confirms the formation of cubic spinel structure of ferrites. The existence of additional peaks at angles (2θ) of 32.93° and 38.40°, shown by stars in Fig. 2.6, indicate the presence of ortho ferrite phases formed due to neodymium content [38]. The presence of ortho ferrite phases are also reported by Gadakari et al. [39] for rare earth doped Mg-Cd ferrites.

Fig. 2.6 X-ray diffractograms for Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 for y = 0) systems

Broadening of peaks in XRD patterns of ferrites under investigation is seen to be greater compared to that reported for Mg-Cd ferrite synthesized with conventional
sintering technique [12]. The lattice constant ‘a’ of all the ferrites under investigations corresponding to prominent (311) plane was calculated by using the Bragg’s relation (2.8). This value of lattice constant was used for determination of inter-planer distance $d_{hkl}$. The calculated values of inter planer distances (d) agree well with each observed values of d.

![X-ray diffractograms for Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 and y = 0.03) systems](image)

**Fig. 2.7** X-ray diffractograms for Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 and y = 0.03) systems

The lattice constant of Mg-Cd (y = 0) and Mg-Nd-Cd (y = 0.03) ferrites with Mg content is presented in **TABLE 2.2**. From this table it is noticed that the lattice constant of both Mg-Cd and Mg-Nd-Cd ferrites decreases with increasing Mg content. This is due to difference in ionic radii of constituent ions. The larger ionic radius Cd$^{2+}$ ions (1.03 Å) are replaced by the smaller ionic radius Mg$^{2+}$ ions (0.78 Å). The similar result was reported for Mg-doped ZnFe$_2$O$_4$ ferrite by Manikandan *et al.* [40]. The table also shows that the lattice constant of Mg-Nd-Cd ferrites are lower than Mg-Cd ferrites. This is due to formation of isolated thin layer around the grain regions by the transmission of Nd$^{3+}$ ions at the grain boundaries instead of entering in to lattice during the sintering process [41]. The similar results are reported by L. Zhao *et al.* [42] for rare earths (La, Nd, Gd) substituted Ni-Mn ferrites, Ladgoankar *et al.* [43] for Nd$^{3+}$ substituted Mg-Zn ferrites and Thankachan *et al.* [26] for Nd$^{3+}$ substituted magnesia. N. Rezlescu and E.
Rezlescu [44] reported the effect of ionic radius of rare earths on lattice constant. They found decreased lattice constant when the rare earth with higher ionic radius was substituted in Ni-Zn ferrite.

### TABLE 2.2
Lattice constants of Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 for y = 0 and 0.03) systems

<table>
<thead>
<tr>
<th>Mg Content (x)</th>
<th>Nd Content (y)</th>
<th>Lattice constants ‘a’ (Å)</th>
<th>Calculated by Bragg’s law</th>
<th>Calculated by Vegard’s Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>8.388</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
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</table>

The lattice constant (a) also obtained by using Vegard’s law for Mg-Nd-Cd ferrites using the relationship [45],

$$a = x \times \text{Lattice const. of Mg ferrite} + (1 - x) \times \text{Lattice const. of Cd ferrite} \quad (2.15)$$

where, x - Mg content

1-x - Cd content

The lattice constant obtained by Vegard’s law for Mg-Nd-Cd ferrites under investigations is also presented in **TABLE 2.2**. It can be seen that the calculated lattice constant and that obtained by Vegard’s law for Mg-Nd-Cd ferrites agree well with each other. The ferrites under investigation obey Vegard’s law.

It is seen that the lattice constant of all ferrites under investigation are smaller than those reported for samples prepared by oxalate co-precipitation [13] and ceramic method [16] under conventional sintering technique. This reduction in lattice constant is due to the lower reaction temperature under microwave sintering technique. T. Sato [46] reported that, the lattice constant of ferrites increases with increase of reaction temperature. He noted that, this exclusive property of co-precipitated ferrite may be due
to the presence of lattice defects and its influence mostly on the surface of ultrafine particles of bulk powder resulting into high surface energy.

The average crystallite size (D) of all the ferrites under investigation was determined by Debye Scherrer formula (2.10) and is presented in TABLE 2.3. It is found that, average crystallite size of Mg-Cd and Mg-Nd-Cd ferrites lies in the range of 38.20 nm to 42.21 nm and 36.93 nm to 40.54 nm respectively. The crystallite size (D) is maximum for composition $x = 0$, then it is decreases up to $x = 0.4$ and then it increases with increase of Mg content for Mg-Cd ferrite. Such trend is not observed for Mg-Nd-Cd ferrite. The average crystallite size of all the ferrites under investigations is larger than those reported by Gadkari et al. [12] for Mg-Cd ferrites prepared by conventional sintering technique. Increased average crystallite size is amazing and also observed by Yadoji et.al. [17]. Yadoji et al. [17] synthesized Ni-Zn ferrites by both conventional and microwave sintering techniques and compare their structural parameters. They inferred that the increase of crystallite size is due to sudden reduction of activation energy by creation of electromagnetic field around the sample [17]. It is revealed that the crystallite size of the ferrites under investigations are larger than those reported for rare earth ($Y^{3+}$) added Mg-Cd ferrites prepared by oxalate co precipitation method using conventional sintering technique [39].

From TABLE 2.3, it is further observed that the crystallite size in Mg-Nd-Cd ferrites is smaller than that for Mg-Cd ferrites. Thus the substitution of Nd$^{3+}$ obstructs the crystal growth in Mg-Cd ferrites [42] as reflected in reduced lattice constant in Mg-Nd-Cd ferrites.

The X-ray density of Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ and $y = 0, 0.03$) system was calculated by using the formula [47],

$$\rho_x = \frac{8M}{N a^2}$$

where, $M$ - Molecular weight

$N$ - Avogadro's number

$'a'$ - lattice constant.

The X-ray density ($\rho_x$) of Mg-Cd and Mg-Nd-Cd ferrites is presented in TABLE 2.3 X-ray density of Mg–Cd and Mg-Nd-Cd ferrites are found to be decreased with increase in Mg content.

By knowing the X-ray and physical densities, the porosities of the ferrites are calculated by using the relation [31]
The porosity of all the ferrites under investigation is presented in TABLE 2.3. It is seen that porosity of Mg-Cd and Mg-Nd-Cd ferrites increases with increase in magnesium content. This is due to replacement of higher density Cd content by lower density Mg content. It is observed that the porosity of Mg-Nd-Cd ferrites lies in the range of 2.277 to 5.036 % and is smaller than that of Mg-Cd ferrites (2.930 to 6.689 %). It is also seen that the porosity and lattice parameter are inversely varied with Mg content.

The Bond lengths (A-O and B-O) and ionic radii (r_A and r_B) on A-site and B-site of the Mg-Cd and Mg-Nd-Cd ferrites are calculated by using Standley’s relations [1] eqns (2.11), (2.12), (2.13), (2.14).

It is observed that, bond lengths (A-O) and ionic radii (r_A) on A-site of Mg-Cd and Mg-Nd-Cd ferrites decrease with increasing in Mg content. This is due to decrease in lattice constant with increase in Mg content [48]. The bond lengths (B-O) and ionic radii (r_B) on B-sites of Mg-Cd and Mg-Nd-Cd ferrites are nearly constant with Mg content. It indicates that the cadmium ions and corresponding replaced magnesium ions occupy A-sites only. The occupancy of cadmium ions on A-sites in Mg-Cd ferrites prepared by ceramic is reported by Karche et al. [16]. Similar result is also reported by Shinde et al. [31] for Ni-Zn ferrites.

### TABLE 2.3
Structural parameters of Mg_xCd_{1-x}Nd_yFe_{2+1/2}O_4 (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 for y = 0 and y = 0.03) systems

<table>
<thead>
<tr>
<th>Mg Content X</th>
<th>Nd Content y</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Crystallite size (D) nm</th>
<th>Grain size (G) μm</th>
<th>X-ray density (ρ_x) gm/cc</th>
<th>Physical density (ρ_y) gm/cc</th>
<th>Porosity (P) %</th>
<th>Bond length ( Å ) A-O</th>
<th>Bond length ( Å ) B-O</th>
<th>Ionic radii (Å) r_A</th>
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2.2.2 SEM Studies

2.2.2.1. Introduction

Surface morphology is an important parameter used for characterization of material. The SEM and FE-SEM are important tools used for morphological studies of the material. They give idea about crystal defects, grain growth and inhomogeneous regions of pore and grain size. The FE-SEM is used to produce especially high resolution images of sample surfaces with size less than 1 nm and wide range of magnification. It gives information about nano sized material.

2.2.2.2. Scanning Electron Microscope (SEM)

This is a basic instrument particularly used for morphological and microstructural characterization. It gives the advantage of improved resolution over optical microscope to analyze the surface of sample. The ray diagram of SEM in form lens focusing system is shown in Fig. 2.8. In the electron microscope, electrons are generated from electron gun by the principal of thermionic emission. Tungsten or lanthanum hexacarbide filaments are normally used as source of thermionic emission. This filament in the electron gun is heated to a very high temperature about 2000-3000 K by passing current through it. When filament is heated, the electrons in it attempt sufficient to be emitted. The mesh around the filament controls the number of electrons coming out from the gun. These electrons are accelerated towards the anode by varying electrostatic field.

The series of electrostatic lenses are used for focusing of electron beam on the sample. Aperture provided with lenses, reduces the extraneous electron from beam and the last lens placed below scanning coil determines the diameter of beam in the form of spot. For achieving higher resolution and depth of field at the cost of brightness, the spot size is made smaller. When a highly accelerated electron beam interacts with the sample, number of signals generated can be captured and displayed as image. When electrons interact with a positive nucleus, they get scattered at broad angles in range from 0°-180°. There are two types of scattered electrons, namely elastically scattered electrons (called back scattered electrons BSE) and inelastically scattered electrons due to interaction with orbital shell electrons (called secondary scattered electrons SSE). The BSE are generally used to produce SEM image. The BSE and SSE are used for the creation of topographical image. On application of positive voltage, the SSE and BSE signals are collected, however on application of negative voltage, only BSE signal is captured as
low energy and SSE signals are repelled. The composed electrons are amplified by photomultiplier to form SEM image. When an exciting electron knocks off inner shell electrons, it results in emission of Auger electrons leading to auger electron spectroscopy.

2.2.2.3. Experimental

The surface morphology of Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 for y = 0, 0.03) systems is investigated by using Mira-3, Tescan, Brno-Czech Republic, Field emission scanning electron microscope (FE-SEM).

2.2.2.4. Results and Discussion

Scanning electron microphotographs of ferrites under investigation in powder form are presented in Fig. 2.9 and Fig. 2.10. From these microphotographs, it is observed that in Mg ferrite, irregular cubic particles are presented along with its small agglomerates. Such result was observed by Bamzai et al. [49] in the characteristic study of Mg-Ca ferrites. The agglomerates of particles are decreased with increase in Mg
content. The grain size in the ferrites under investigation is calculated by using average linear intercept method [50] using the equation,

\[
G_a = \frac{1.5L}{MN}
\]

where, \( L \) = Length of test line in cm
\( N \) = Total no. of Intercepts.
\( M \) = Magnification.

Fig. 2.9. SEM images \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\( x = 0, 0.2, 0.4, 0.6, 0.8, 1 \) for \( y = 0 \)) system

The average grain size of \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\( x = 0, 0.2, 0.4, 0.6, 0.8, 1 \) and \( y = 0, 0.03 \)) systems is presented in TABLE 2.3. It is seen that, grain size of the ferrites is much larger than that reported for \( \text{Mg-Cd} \) (\( y = 0 \)) ferrites prepared by conventional sintering technique [12]. It is also found that, the average grain size of \( \text{Mg-Nd-Cd} \) (\( y = 0.03 \)) ferrite initially increases with increasing Mg content up to \( x = 0.6 \) and decreases for increase in \( x \) (compositions \( x = 0.8 \) and 1). It is also observed that grain sizes of the \( \text{Mg-Nd-Cd} \) ferrites is higher than those reported for rare earth added \( \text{Mg-Cd} \) ferrites prepared
by oxalate co-precipitation method using conventional sintering technique [39]. The microwave induced field plays an important role in promoting densification process due to increasing mobility of defusing ions across boundaries of grains which influences grain growth. According to absolute rate reaction theory, higher values of net growth process with microwave field is favorable for formation of larger grains [17].

Fig.2.10. SEM images Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 for y = 0.03) system.

From TABLE 2.3, it is observed that the grain size of Mg-Nd-Cd ferrite is lower as compared that for the Mg-Cd ferrite [39]. The similar result is reported for Y$^{3+}$ added Mg-Cd ferrites[39], Sm$^{3+}$ dopedd Mg – Cd ferrites [51] and Nd$^{3+}$ substituted Ni–Zn ferrites[41]. This clearly points out that, the substitution of 0.03 mol of neodymium reduces on the grain growth of ferrite by 33%.
2.2.3 Energy Dispersive Analysis of X-Ray (EDAX) Studies

2.2.3.1. Introduction

The energy dispersive X-ray spectroscopy is mostly used for the analysis of ions in material. When X-rays are bombarded on sample, various peaks corresponding to respective metal ions are observed. The percentage of elements present in the material is observed.

The EDAX systems consist of a sensitive X-ray detector and liquid nitrogen. The detector is mounted at the ending of an arm in sample chamber of an instrument, which itself is frozen in liquid nitrogen. The ordinary detectors are made of Si (Li) crystals working at lower voltages to raise sensitivity [52-54]. The software provided collects the data related to ions present in the sample and sketches energy spectra of the material.

2.2.3.2 Experimental

The typical energy dispersive X-ray analysis (EDAX) spectrum for \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\(x = 0.0, 0.4\) for \(y = 0, 0.03\)) are recorded at room temperature. EDAX spectrum for \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\(x = 0, 0.4\) for \(y = 0, x = 0.2, 0.4\) for 0.03) are shown in Fig.2.11 and Fig.2.12.

![Fig.2.11 EDEX image of \( \text{Mg}_x\text{Cd}_{1-x}\text{Nd}_y\text{Fe}_{2-y}\text{O}_4 \) (\(x = 0, 0.4\) for \(y = 0\))](image)

2.2.3.3 Results and Discussion

This gives quantitative estimation of elements obtained from spectrum through its weight and atomic percentages. The results shows the presence of the respective elements in the desired composition with all the peaks corresponding to elements such as Mg, Fe, O, and Cd there by suggesting the formation of pure CdFe and MgCdFe and Mg, Fe, O, Nd and Cd confirming the formation of Mg-Cd (\(y = 0\)) and Mg-Nd-Cd (\(y = 0.03\)) ferrites.
2.2.4 Fourier Transformation Infrared Spectroscopy (FTIR) Studies

2.2.4.1 Introduction

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds. Signal to noise ratio is improved by using modern FT-IR instruments.

2.2.4.2 Fourier Transformation Infrared Spectroscopy

The block diagram of double beam spectrophotometer in the form ray diagram is shown in Fig. 2.14. In this case the beam is split into two parts; one is directed through the sample cell and the other through the reference cell. The two beams are then compared either continuously or alternately.

The basic components of an IR spectrophotometer are
1. Source of radiation
2. The fore optics
3. Monochromator
4. Detector with an amplifier
5. Recorder

1. Source of radiation

The source is in the form of black body radiator. Commonly used sources are the globar filament and the Nernst glowers. The Nernst glower consists of a spindle of rare earth oxides of about 2.5 cm long and 0.25 cm diameter with black body peak around 1.4
µm at 1600 -1700 °C and useful in the shorter wavelengths. The globar consist of rod of silicon carbide usually about 5 cm in length and 0.5 cm in diameter with black body peak between 1.8 to 2.0 µm at 1200 °C and useful in the longer wavelengths.

**Fig. 2.13** Schematic diagram of IR spectrometer

2. **The fore optics**

It consists of the source, mirrors M₁, M₂ and a rotating mirror/chopper M. M₁ and M₂ divide the source radiation into two equivalent beams. One of which passes through the sample and the other passes through an equivalent path and is called the reference beam. These two beams meet at the rotating sector mirror/chopper. The rotating mirror M alternately done two functions, one allows or reflection of the reference beam with a fixed period to the monochromatic slit and other is passing of the sample beam through the spaces.

3. **Monochromator**

It is used to splits the polychromatic radiations obtained from mirror M into its component wavelengths. The grating or prism is used as a monochromator. Rock salt prism is usually used as monochromator in the region 650 to 4000 cm⁻¹.

4. **Detector**

Thermopiles, bolometer, thermister, photoconductive materials, Golay cells etc. are used as detectors. Golay cell is a thermal detector. In this case radiation falls onto a very small cell containing air and the temperature changes are measured in terms of pressure changes within the cell. In case of photo detector, the radiation is allowed to fall
on photo conducting material and the conductivity of the materials is measured continuously by a bridge network. The signal is then fed to a high gain amplifier which amplifies the low intensity signal.

5. Recorder

An attenuator moved by amplified signal, cuts the radiation coming out of the reference beam until energy balance is restored. This is achieved by a motor which drives the comb into the reference beam when an absorbing band is encountered and out of the beam when the band is passed over. The recorder pen is also coupled to this motor so that the comb movement is followed exactly by the pen.

2.2.4.3 Experimental

The FTIR spectra of the Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 for y = 0, 0.03) systems are obtained in the range of 350 cm$^{-1}$ - 800 cm$^{-1}$ using Perkin-Elmer FTIR spectrum one spectrometer by using KBr pellet technique.

2.2.4.4 Results and Discussion

Fourier transform infrared absorption spectra of Mg$_x$Cd$_{1-x}$Nd$_y$Fe$_{2-y}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 for y = 0, 0.03) systems are shown in Fig. 2.14 and Fig.2.15. The presence of two major absorption bands near about 600 cm$^{-1}$ and 400 cm$^{-1}$ in the range of wave numbers 350-800 cm$^{-1}$ indicates the well formation of ferrites. Such band positions are the fundamental characteristics of spinel ferrites suggested by Waldron [55]. The absorption band at $v_2$ is due to stretching of metal-oxygen at tetrahedral site (M$_\text{tetra}$$\leftrightarrow$O) and absorption band at $v_4$ is due to the stretching at octahedral site (M$_\text{octa}$$\leftrightarrow$O). [56-57]. White et al. [58] suggested four IR active bands in spinel ferrites, denoted as $v_1$, $v_2$, $v_3$, $v_4$ with descending wave numbers. The existence of these four bands in normal and inverse spinels structure has been rationalized on the basis of group theoretical calculations employing space groups and point symmetries. Preudhomme et al. [59] also reported that four bands among the first three bands are fundamental bands. They are due to the tetrahedral and octahedral complexes, whereas the fourth band is due to various types of lattice vibrations.

The wave numbers corresponding to absorption bands of all the ferrites under investigation are tabulated in TABLE 2.4, where they labeled as $v_1$, $v_2$, $v_3$, $v_4$, $v_5$ and $v_6$ in the sequence of decrease wave numbers. The wave numbers ($v_2$) and ($v_4$) are corresponding to higher and lower absorption bands. It is observed that $v_2$ and $v_4$ for Mg-Cd (y = 0) ferrites lies in the range 561-582 cm$^{-1}$ and 425-437 cm$^{-1}$ respectively and that
for Mg-Nd-Cd (y = 0.03) ferrites lies in the range 559-581 cm\(^{-1}\) and 424-458 cm\(^{-1}\) respectively, confirming the good formation of spinel ferrites.

Fig. 2.14 FTIR spectra of Mg-Cd ferrite for y = 0

Fig. 2.15 FTIR spectra of Mg-Nd-Cd ferrite for y = 0.03
From **TABLE 2.4**, it is also seen that, there is no any notable variation in $\nu_4$ except $x = 0.2$ whereas the values of $\nu_2$ increases with increase in Mg content for Mg-Cd ferrite. The variations in band location are because of the difference in the Fe$^{3+}$- O$^{2-}$ distances for the octahedral and tetrahedral complexes [57]. This also suggests that Mg$^{2+}$ occupies A-site and is in good agreement with our XRD results. From spectra, it is also observed that the broadening as well shoudering in absorption bands corresponding to tetrahedral site are decreased with increase in Mg content. This may be due to decreasing concentration of Fe$^{2+}$ ions by increasing Mg$^{2+}$ ions. Behavior of shoudering appears in the lower frequency absorption bands may be due to increasing concentration of Fe$^{3+}$ ions due to microwave sintering technique used under investigation.

For Mg-Nd-Cd ferrites (Fig 2.16), it can be observed that, with increasing Mg content (up to $x = 0.6$), the wave number increases and thereafter (above $x = 0.8$) decreases. This is attributed to variations of grain size with Mg content. From this table it is further observed that wave numbers corresponding to lower frequency absorption band slightly shift towards lower wave number side with increasing Mg content.

**TABLE 2.4**

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<td>0.2</td>
<td>0.03</td>
<td>573</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>0.03</td>
<td>574</td>
<td>507</td>
</tr>
<tr>
<td>0.6</td>
<td>0.03</td>
<td>696</td>
<td>581</td>
</tr>
<tr>
<td>0.8</td>
<td>0.03</td>
<td>694</td>
<td>576</td>
</tr>
<tr>
<td>1</td>
<td>0.03</td>
<td>693</td>
<td>565</td>
</tr>
</tbody>
</table>

This is due to lowered concentration of Fe$^{3+}$ ions with increase in Mg content [38]. The broadening on A-sites was increased with Mg content ($x$) in Mg-Nd-Cd ferrite [38] as compared that in Mg-Cd ferrite [30]. Fig.2.15 shows additional lower intense bands ($\nu_1$, $\nu_3$, $\nu_5$ and $\nu_6$) as well as shoudering appearing around the two main bands due to changed percentage of Fe$^{3+}$ ions in the Mg-Nd-Cd ferrites. These bands are not
observed in Mg-Cd ferrite. These lower intense bands were explained in following paragraph.

The low intensity absorption band corresponding to $\nu_1$ is observed in range of wavenumbers 638-696 cm$^{-1}$ for composition $x = 0, 0.6, 0.8$ and 1. The similar locations of such bands, but with high intensity were observed in IR study of number of cubic normal II-III spinels [58]. The $\nu_3$ for composition $x = 0.4, 0.6, 0.8, 1$ and $\nu_5$ for composition $x = 0, 0.2, 0.4$ corresponding to shoulder near the two main bands $\nu_2$ and $\nu_4$ respectively may be due to changed percentage of Fe$^{3+}$ ions in the ferrites under investigation. The last band corresponding to $\nu_6$ observed for Mg-Nd-Cd ferrite in range of wavenumbers 385-391 cm$^{-1}$ may be due to various lattice vibrations under the experimental conditions [58]. Such band was reported in nearly similar range of wavenumbers by Ravinder [60] in the study of far-infrared spectrum of mixed Li - Zn ferrites.
References


[31] T. J. Shinde, A. B. Gadkari, P. N. Vasambekar, “Saturation magnetization and structural analysis of Ni$_{0.6}$Zn$_{0.4}$Nd$_{y}$Fe$_{2−y}$O$_{4}$ by XRD, IR and SEM techniques”. *J. of Mater. Sci: Mater Electr.*, vol. 21, no.2, pp. 120-124, 2010.


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