CHAPTER 5

STUDY OF CoFe₂O₄ PARTICLES SYNTHESIZED WITH PVP AND CITRIC ACID

This chapter deals with the synthesis of CoFe₂O₄ particles using metal nitrates, PVP and citric acid. The structure, morphology and the magnetic properties of the resultant cobalt ferrite powders synthesized with various concentrations (3, 6, 9 and 15 wt%) of PVP along with CA are presented. These powders are compared with the CoFe₂O₄ powders synthesized by a similar procedure with the same PVP concentrations, without the CA. This chapter examines how the inclusion of CA in the sol–gel precursors, affects the size and magnetic properties of the resultant CoFe₂O₄ powder. CA acts as a chelating agent and forms metal citrate complexes reacting with the PVP. The FT-IR and TG/DSC analyses confirm the chelates’ formation. These complexes reduce the rate of formation of CoFe₂O₄ and decrease the particle size. The HR SEM images and their corresponding histograms testify the results.

5.1 INTRODUCTION

One of the controversial issues in the magnetic behaviour of nanoparticles is the observed variation of saturation magnetization ($M_s$) with respect to the bulk materials [83]. In the spinel ferrites MeFe₂O₄, where Me is a divalent cation, the cation distribution between the tetrahedral (Td) and octahedral (Oh) sites of the close-packed oxygen structure affects the magnetic properties of the particles, e.g., saturation magnetization and magnetic anisotropy [84, 85]. The cation distribution is usually expressed in terms of the inversion degree ($\gamma$), defined as the fraction of divalent ions in octahedral sites [86]. In this chapter, the influence of the chelating effect on the magnetic behaviour of final products is studied.
5.2 CHELATING EFFECT

Chelation is the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. Usually, these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The chelate effect describes the enhanced affinity of the chelating ligands for a metal ion, compared to the affinity of a collection of similar non-chelating (monodentate) ligands for the same metal. Chelation basically creates a ring structure around metal ions, preventing them from combining with other metal ions, that would otherwise result in insoluble formations. One such chelating agent is EDTA, ethylene-diamine tetra-acetic acid, which exhibits a six-point binding to metals (Figure 5.1)

![Figure 5.1 Ethylene diamine chelate](image)

Examples:

Virtually all biochemicals exhibit the ability to dissolve certain metal cations. Proteins, polysaccharides, and polynucleic acids are excellent polydentate ligands for many metal ions. Organic compounds such as the amino acids, glutamic acid and histidine, organic diacids such as malate, and polypeptides such as phytochelatin are also typical chelators.
Applications:

Chelation effects are utilized in various industries that include cleaning, water treatment, metal working and the prevention of mineral deposit spotting of plants grown in nurseries and agricultural applications. Chelating agents such as EDTA salts are used in medicine to remove toxic metals (e.g., LEAD, CADMIUM) from the body. The iron-binding PORPHYRIN group in HEMOGLOBIN, the magnesium-binding porphyrin in CHLOROPHYLL and the cobalt-binding porphyrin in vitamin B are natural chelators.

The phenomenon of the chelate effect is a firmly established empirical fact and citric acid is employed as the chelating agent in this research work.

5.3 EXPERIMENTAL

5.3.1 Materials and methods

AR grade Fe (NO₃)₃·9H₂O, Co (NO₃)₂·6H₂O, citric acid in the molar ratio of 2:1:1 and PVP (MW=40,000) were used. Aqueous solution of citric acid and PVP (3 wt% concentration) was prepared separately and mixed with ferric nitrate and cobalt nitrate solution. The resultant mixture was stirred continuously to get a clear solution. This solution was heated to 90 °C and subsequent stirring led to gel formation. The gel was kept in hot air oven for 2 days at 120 °C to evaporate remaining water.

5.3.2 Characterisation

The TG/ DSC analysis was done on the acquired solid using NETZSCH STA-409 C/CD in a static air atmosphere. The FT-IR spectrum (500 – 4000 cm⁻¹) was recorded on a PerkinElmer Spectrum One spectrophotometer with KBr pellets. The procedure was repeated for the same molar ratio of ferric nitrate, cobalt nitrate and citric acid, with various PVP concentrations of 6, 9 and 15 wt%. All the samples were then calcinated at 640 °C for 2 h and crushed to form a fine powder. The samples synthesized with 3, 6, 9, and 15 wt% of PVP concentrations were then
named as samples A, B, C and D respectively. The phase structural analysis of the calcined powder was identified using the X-ray diffractometer (PANalytical X’pert pro) of wave length ($\lambda=0.15406$ nm) in a wide range of 20 ($20^\circ < \theta < 70^\circ$). The morphology and dispersibility of the products were measured by the HR-SEM (FEI Quanta 200FEG). The magnetic parameters of the cobalt ferrite powder were measured by a Vibrating Sample Magnetometer (VSM) - Lakeshore 7304, with a maximum field of 15,000 Gauss (G) at room temperature.

5.4 RESULTS AND DISCUSSION

5.4.1 Thermal analysis of the gel

![Figure 5.2 TG / DSC curve for the CA-PVP gel](image)

In the TG/ DSC curves as shown in Figure 5.2, the mass loss of 7.5 % from room temperature to 500 °C is due to the gradual burning of the polymer network along with the dehydration and decomposition of nitrates. The mass loss in the temperature range of 500 – 600 °C, accompanied by a small endothermic curve,
is due to the burning of metal citrates. The larger endothermic event from 700 °C depicts the formation of CoFe₂O₄ particles.

Figure 5.3 FT-IR spectrum of the CA-PVP gel

5.4.2 FT-IR Spectrum Analysis

Characteristic bands are observed at 3393, 2920, 2851, 2333, 1623, 1383, 570, 494 cm⁻¹ (Figure 5.3). The band at 3393 cm⁻¹ is due to the presence of the –OH group stretching vibration mode. The bands at 2920 and 2851 cm⁻¹ are due to aliphatic C-H stretching groups [76]. The presence of bands at 1623 and 1383 cm⁻¹ confirm the asymmetric and symmetric vibrations of the COO⁻ groups respectively [49]. The band at 570 cm⁻¹ is due to Tetrahedral (Fe-O) vibration and the band at 494 cm⁻¹ is due to Octahedral (Co-O) vibrations, typical characteristics of spinel ferrites [76]. This analysis confirms the presence of metallic citrates formed due to the chelation process.
5.4.3 XRD analysis

All the XRD patterns (Figure 5.4a-d) show typical reflections at 2θ values of 30°, 35°, 43°, 53°, 57°, and 63° are assigned to (220) (311) (400) (422) (511) (440) planes respectively (JCPDS Card No: 22-1086). They belong to the cubic spinel structure of the CoFe₂O₄ particles. It is worthwhile to note that the impure phases observed for the CoFe₂O₄ samples synthesized from the PVP gel at 9 and 15 wt concentrations [Figure 4.3(c, d)] are totally absent in all the samples synthesized from the CA-PVP gel. The reduction in FWHM of standard diffraction peaks of these samples, when compared to the samples synthesized from PVP gel for similar concentrations, signifies that CA has aided the formation of finer particles of CoFe₂O₄.

Figure 5.4 (a-d) XRD patterns of CoFe₂O₄ powder synthesized from CA-PVP gel with different PVP concentrations. (a) 3 wt%, (b) 6 wt%, (c) 9 wt%, and (d) 15 wt%
The probable distribution of metallic citrates and metallic ions in the polymer cavities is shown in Figure 5.5. It is observed from the FTIR that CA acts as a chelating agent and forms metal citrate complexes from metal nitrates. The metal citrate complexes [87, 88] are bulkier compared to the metal ions. During the calcination, the bulkier cobalt/ferric citrates would move slowly and provide ample time for the ions to occupy exact positions in the crystal lattice, unlike the fast migration of lighter cobalt/ferric ions in the PVP gel. This has led to an efficient disagglomeration in the CoFe$_2$O$_4$ samples synthesized with CA.

![Figure 5.5 Distribution of metallic citrates and metallic ions in the cavities of the PVP matrix](image)

### 5.4.4 Morphological analysis

The HR-SEM images (Figure 5.6a–d) show the size, shape and agglomeration of CoFe$_2$O$_4$ samples synthesized from the CA-PVP gel with various PVP
concentrations. It is observed from the images that with the increase of PVP concentration from 3 to 15 wt%, the particle sizes are reduced significantly. This is confirmed by the respective histograms (Figure 5.7 a-d). The bars representing the particle counts are shifted toward smaller crystallite sizes with the increase of PVP concentration. When the HR-SEM images of cobalt ferrites synthesized with CA (Figure 5.6a-d) and without CA (Figure 4.4a-d) are compared, it is observed that, CA due to its chelating effect has considerably reduced the particle sizes for the respective PVP concentrations. The HR-SEM image of the CoFe₂O₄ powder for 3 wt% PVP in the absence of CA has large particles, as a result of the agglomeration of the spherical particles; i.e., sizes of upto 1 μm (Figure 4.4a). When CA is included in the sol–gel process with the same PVP concentration, the

Figure 5.6 (a-d) HR-SEM images of CoFe₂O₄ powder synthesized from CA-PVP gel with different PVP concentrations (a) 3 wt%, (b) 6 wt%, (c) 9 wt%, and (d) 15 wt%
particle sizes are considerably reduced. This is probably because of the presence of the ester groups in the CA-PVP gel. The particle size reduction may be explained in the following manner. The metal citrate complexes are bulkier relative to metal nitrates. During the calcination process, the metal citrate complexes slowly form CoFe$_2$O$_4$ particles, after the burning of the polymeric network. This leads to an efficient disagglomeration and reduced particle sizes (Figure 5.6a). The particle size reduction with increase in surfactant concentration is shown in respective histograms (Figure 5.7a-d) of HR-SEM images (Figure 5.6a-d).

Figure 5.7 (a-d) Histograms of HR-SEM images of CoFe$_2$O$_4$ powder synthesized from the CA-PVP gel with different PVP concentrations (a) 3 wt% (b) 6 wt% (c) 9 wt% and (d) 15 wt%
5.4.5 Role of Citric Acid

To summarize, CA reduces the kinetics of the formation of cobalt ferrites by acting as a chelating agent. Thus, CA forms metal citrate complexes as seen from the FTIR analysis. The bulkier metal citrate complexes, owing to their masses, migrate slowly, during the formation of CoFe$_2$O$_4$ particles. CA’s metal ion chelating abilities brought about changes in the kinetics of CoFe$_2$O$_4$ particle’s growth formation, prevented particle agglomeration and reduced the particle’s diameter. The effective reduction of particle sizes is observed, comparing Figure 5.6a and Figure 4.4a.

5.4.6 Magnetic properties

![Hysteresis loops](image)

Figure 5.8 Hysteresis loops of the samples synthesized from the CA-PVP gel with different PVP concentrations (a) 3 wt% (b) 6 wt% (c) 9 wt% and (d) 15 wt%
Cobalt ferrite is one of the most promising candidates among spinel ferrites for high-density recording media such as audio and videotape, high-density digital recording disks, magnetic fluids, data storage, magnetic drug delivery, medical applications, including radio-frequency hyperthermia, photomagnetics, magnetic resonance imaging (MRI) medical diagnostics, microwave devices, magneto-optics devices, sensors, high frequency applications and catalysis [89-92]. To clarify its application, the magnetic hysteresis loops for the CoFe$_2$O$_4$ powder, that is synthesized with various PVP concentrations are measured at room temperature (Figure 5.8). The magnetic properties are listed in Table 5.1, and indicate the presence of an ordered magnetic structure for the spinel system.

Table 5.1 Comparison of magnetic properties of samples synthesized from PVP and CA-PVP gel.

<table>
<thead>
<tr>
<th>PVP concentration</th>
<th>samples synthesized without CA*</th>
<th>samples synthesized with CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Grain size nm</td>
<td>$H_c$ [kA/m]</td>
</tr>
<tr>
<td>3 wt%</td>
<td>442</td>
<td>58.7</td>
</tr>
<tr>
<td>6 wt%</td>
<td>409</td>
<td>64.1</td>
</tr>
<tr>
<td>9 wt%</td>
<td>351</td>
<td>52.6</td>
</tr>
<tr>
<td>15 wt%</td>
<td>303</td>
<td>66.1</td>
</tr>
</tbody>
</table>

*Reference [75].

Cation distribution is usually expressed in terms of the degree of inversion ($\gamma$), defined as the fraction of divalent ions in octahedral sites [93]. The migration of cobalt ions to octahedral sub-lattice increases $\gamma$. Saturation magnetization ($M_s$) in spinel ferrites is intrinsically connected with the cation occupancy of interstitial sites and spin arrangement [93]. The octahedral site in the spinel structure has six nearest tetrahedral sites, which are occupied by six Fe ions in full inverse spinel and by 6, 5, 4, or 3 Fe ions in a partially inverse structure [94].
Samples synthesized without CA illustrate large variations in $M_s$ values for various PVP concentrations (Table 5.1). The $M_s$ value for 3 wt% PVP is 50.8 Am$^2$/kg; and, it is increased to 81.1 Am$^2$/kg for 15 wt % PVP. Zit et al. [90] have reported that the variation of saturation magnetization can occur due to the rearrangement of the cation distribution and change in degree of CoFe$_2$O$_4$ inversion, where an exchange of Co$^{2+}$ and Fe$^{3+}$ ions from the octahedral and tetrahedral sites and vice versa takes place. The significant change in the $M_s$ values may be due to the inconsistency in ($\gamma$) caused by the PVP gel. On the contrary, in the samples synthesized from the CA-PVP gel, such drastic variations in $M_s$ are minimised. The addition of CA has contributed to the consistency in $M_s$ values, probably by maintaining the same degree of inversion ($\gamma$). The chelating effect of CA led to an orderly distribution of magnetic cations and increased the saturation magnetisation values. The lower coercive values $H_c$ of the samples A (50 kA/m) and C (57.3 kA/m) might be due to complex factors such as exchange anisotropy due to spin disorder at the particle interface, residual strain, defects and nature of the surface.

5.5 CONCLUSION

The novel sol-gel route aided by chelation of metal ions can also be adopted for preparing other functional ferrite materials. The evolution of the chemical constitution, structure and magnetic properties during the sol-gel process was systematically studied. Effect of CA as a chelating agent on the phase-stability, morphology, microstructure and crystallite size of sol-gel synthesised CoFe$_2$O$_4$ particles was studied. CA facilitates the solid state reaction between Co and Fe oxides yielding metal citrate complexes, preventing them from combining other metal ions and effectively disagglomerated the cobalt ferrite particles. The size of the nanoparticles decreased with increase in PVP concentration due to the enhancement of the polymer matrix. The consistency in magnetic saturation values suggests the vital role of the chelating agent.