CHAPTER 6

SYNTHESIS OF CoFe$_2$O$_4$ POWDER VIA PVA ASSISTED SOL-GEL PROCESS$^2$

This chapter discusses the synthesis of CoFe$_2$O$_4$ ferrites with metal nitrates as the precursors and PVA as the surfactant. The concentration of the surfactant was varied; namely, 3, 6, 9 and 15 wt%. The resultant ultrafine ferrite powders have been characterized by X-ray diffraction, thermal gravimetry, differential scanning calorimetry and room temperature magnetic studies. The morphology of the powder was identified by high resolution-scanning electron microscopy. Increase in the PVA concentration led to a decrease in the particle size. X-ray diffraction results indicate that the resultant CoFe$_2$O$_4$ crystallites consist of a spinel phase. Significant differences in the magnetic properties of CoFe$_2$O$_4$ samples synthesized with various concentrations of PVA were observed. The magnetisation measurements show that when the PVA concentration increased, coercivity initially decreased, and then increased, whereas retentivity and magnetisation decreased. The optimum concentration of PVA for the synthesis of CoFe$_2$O$_4$ ferrites with high coercivity and moderate saturation magnetisation, is obtained from this investigation.

6.1 INTRODUCTION

The sol-gel process is a liquid phase synthesis, involving hydrolysis and condensation reactions of metal precursors, leading to the formation of three-dimensional inorganic networks. The process is simple, uses low cost starting materials, yields fine microstructure, homogeneous, narrow particle size distribution

$^2$ A part of this work is reported in “Sivakumar et al., 2012, J Mater Sci: Mater Electron., 23(5), pp. 1045-1049”.
and is considered an environmentally friendly method that offers scalability for large scale production. In this work, we attempted to synthesize CoFe_2O_4 particles with excellent magnetic properties by the sol-gel method using PVA as the surfactant in various concentrations, namely, 3 wt%, 6 wt%, 9 wt% and 15 wt%.

The synthesized compounds were systematically and quantitatively characterized for ferrite formation, crystallite size, microstructure and magnetic properties. Evaluation and characterization tools including X-ray diffraction (XRD), scanning electron microscope (SEM) and a vibrating sample magnetometer (VSM) were used to identify the effect of surfactant’s concentration and its impact on crystallite size and magnetic properties of the formed powders. With this knowledge a base for understanding the impact of each concentration on product properties can be established.

Polyvinyl alcohol was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide. Polyvinyl alcohol is an odourless and tasteless, translucent, white or cream coloured granular powder. Its structural formula is shown in Figure 6.1.

![Figure 6.1 Structural formula of PVA](image)

Polyvinyl alcohol has various applications in the food industries as a binding and coating agent. As a component of tablet coating formulations intended for products including food supplement tablets, Polyvinyl alcohol protects the active ingredients from moisture, oxygen and other environmental components, while simultaneously masking their taste and odour. The viscosity of polyvinyl alcohol
allows for the application of the polyvinyl alcohol coating agents to tablets, capsules and other forms to which film coatings are typically applied at relatively high solids contents. PVA can be cross-linked through the use of difunctional cross-linking agents. The crystalline nature of PVA has been of specific interest. Poly(vinyl alcohol) has been examined for numerous applications.

6.2 EXPERIMENTAL TECHNIQUES

6.2.1 Materials and methods

The chemicals used to synthesize CoFe$_2$O$_4$ powders were Co(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.9 H$_2$O, and Polyvinyl Alcohol (PVA). All these chemicals were of an analytical grade, and used without purification. The PVA solution was prepared by slowly sprinkling PVA powder in deionized water, under continuous stirring to avoid clumping of the material in water. The sols were prepared by dissolving ferric nitrate and cobalt nitrate in deionized water in the stoichiometric ratio of 1:2. After constant stirring for 1h, the PVA solution was added to the sols. The subsequent mixture was then heated to 90 °C and subjected to constant stirring, till a gel was obtained. The gel was then kept in a hot air oven for 2 days to evaporate water. The precursor was then calcined at 960 °C for 2 h. Afterwards it was crushed for 30 minutes in a mortar to form a powder. Four samples A, B, C, D were synthesized in this way, with various PVA concentrations of 3wt %, 6wt%, 9 wt% and 15wt% respectively, the rest of the procedure being the same.

6.2.2 Characterisation

The precursor of sample A was subjected to the TG/DSC analysis between 28 °C and 1200 °C by NETZSCH STA 409 C/CD in a static air atmosphere, at a heating rate of 10 °C per minute. The FT-IR spectrum (500 – 4000 cm$^{-1}$) was recorded on a PerkinElmer Spectrum One spectrophotometer with KBr pellets. The crystalline phases present in the calcinated samples were identified by X-ray diffraction (XRD) on a PANalytical X’pert pro diffractometer using CuK$_\alpha$ ($\lambda=0.15406$ nm) in the range 20 from 20° to 80°. The morphology and dispersibility
of the products were measured by the HR-SEM (FEI Quanta 200FEG). The magnetic properties of the samples were characterized using a vibrating sample magnetometer (VSM; Lakeshore 7304) at room temperature in a maximum applied field of 20 kG.

6.3 RESULTS AND DISCUSSION

6.3.1 Thermal decomposition of the gel

![Figure 6.2 TG/DSC curves of the precursor heated from room temperature to 1198 °C at a rate of 10 °C per minute under air](image)

Figure 6.2 TG/DSC curves of the precursor heated from room temperature to 1198 °C at a rate of 10 °C per minute under air

TG / DSC curves of the gel precursor are shown in Figure 6.2. Five stages of weight loss are observed in the TG curve. The first thermal event in the temperature range of 25–190 °C, with the mass loss of 17.4 %, is associated with the loss of water molecules which is characterised by an endothermic peak in DSC analysis. The second stage in the range of 190–230 °C in TG curve, with a mass loss of 12.6%, is due to spontaneous combustion caused by interactions of the nitrate ions in the gel. This is accompanied by an exothermic event in DSC analysis. The third stage in TG curve, in the temperature range of 230–290 °C, with the mass loss of 9.6%, is caused by the polymeric chain decomposition of PVA [95]. The fourth stage in the temperature range of 290–330 °C, with the mass loss of 3.4% is due to
the loss of structural water. The final stage in the temperature range of 330–842 °C, accompanied by a mass loss of 2.2%, is due to the further thermal decomposition of residual compounds and the onset of crystallisation process. Above 842 °C no weight loss was observed and the crystallisation process was completed. The endothermic peak observed at 306 °C in DSC curve confirms the oxidation combustion of PVA main chain and another small endothermic peak observed at 826 °C is due to further decomposition of the nitrates. A broad endothermic event observed in the DSC curve between 870 and 1,200 °C is due to the densification of the powder. In the TG curve no weight loss is observed above 842 °C, which means that pure ferrites could be observed above that temperature.

6.3.2 FT-IR analysis

Figure 6.3 FT-IR spectrum of the PVA gel
Table 6.1 The observed characteristic IR bands of the PVA gel [76, 82]

<table>
<thead>
<tr>
<th>Wave number cm⁻¹</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3357</td>
<td>( \nu_s ) (O-H)</td>
</tr>
<tr>
<td>1642</td>
<td>( \nu_s ) (H-O-H) free or absorbed water</td>
</tr>
<tr>
<td>1412</td>
<td>( \nu_{as} ) (NO₃⁻)</td>
</tr>
<tr>
<td>1358</td>
<td>( \nu_b ) (O-H)</td>
</tr>
<tr>
<td>1313</td>
<td>( \nu_b ) (O-H)</td>
</tr>
<tr>
<td>1087</td>
<td>( \nu_s ) (C-O-C) dehydration of O-H group from PVA</td>
</tr>
<tr>
<td>802</td>
<td>( \nu ) Ferrite tetrahedral (Fe-O)</td>
</tr>
<tr>
<td>697</td>
<td>( \nu ) Ferrite tetrahedral (Fe-O)</td>
</tr>
<tr>
<td>500</td>
<td>( \nu ) Ferrite Octahedral (Co-O)</td>
</tr>
<tr>
<td>490</td>
<td>( \nu ) Ferrite Octahedral (Co-O)</td>
</tr>
</tbody>
</table>

6.3.3 X-ray Diffraction studies

The XRD patterns of the CoFe₂O₄ powder synthesized with 3, 6, 9 and 15 wt% of PVA concentration are shown in Figure 6.4a-d respectively. The prominent peaks observed at 2θ values of 30°, 35°, 37°, 43° and at 57° are assigned to (220), (311), (400), (511), (440) planes respectively.
Figure 6.4 XRD patterns of CoFe$_2$O$_4$ powder synthesized by the sol-gel method with different PVA concentrations (a) 3 wt% (b) 6 wt% (c) 9 wt% (d) 15 wt%

All these peaks confirm the cubic spinel type lattice of CoFe$_2$O$_4$ which matches well with the standard XRD pattern (JCPDS Card No: 22-1086). No additional peaks were observed in these XRD patterns, suggesting that no other phases besides cobalt ferrite structure are detected in all the samples. This is also in good agreement with the results deduced from the TG/DSC curve that above 842 °C no sharp endothermic curve was observed, signifying that the pure phase of CoFe$_2$O$_4$ has started above that temperature. Comparing Figure 6.4a-d, we observe that the intensity of the peaks increases with increasing PVA concentration, which suggests that the addition of PVA significantly increased the crystallinity and composition of CoFe$_2$O$_4$ particles. The three dimensional network structure of PVA acts like a confined space that allows sufficient contact and reaction of the reactants and also limits the growth of the CoFe$_2$O$_4$ particles, leading to the formation of CoFe$_2$O$_4$ particles of good crystallinity and high dispersibility [73].
6.3.4 **Morphological Analysis**

Figure 6.5a-d shows the HR-SEM images of the samples with various PVA concentrations. It can be seen from the micrographs that there are significant differences in the microstructures of the four samples. Figure 6.5a reveals that the CoFe$_2$O$_4$ particles prepared with 3 wt% of PVA show the presence of very large lumps which are agglomerates of small spherical particles. The maximum agglomeration size extends even up to 1 μm. Within a single agglomerate, the particles are close-packed and supposed to interact strongly, yielding high magnetisation. For the sample with 6 wt% of PVA concentration, the CoFe$_2$O$_4$ particles are dispersed and crystallites of sizes in the range of 100-500 nm are present. As seen from Figure 6.5c, it is clear that the particles are dispersed again and the individual particle size is further reduced. From Figure 6.5d it is observed that the individual particles are more prominent, with the crystallite sizes further reduced in the range of 50 to 150 nm. In this case, smaller crystallites are predominantly present in comparison with Figure 6.5a-c. Considering all these facts, it is concluded that for the samples with increasing PVA concentration, the particle agglomeration tendencies decrease and there are significant variations in the grain size. The increase of the PVA chains breaks up the network structure of agglomerated crystallites and results in the formation of dispersive CoFe$_2$O$_4$ particles of lesser grain size [73]. It is evident that the size, shape and agglomeration state of the as-prepared CoFe$_2$O$_4$ particles in Figure 6.5d are better than those in Figure 6.5a-c. The histograms of HR-SEM images shown in Figure 6.5a–d are presented in Figure 6.6a–d. From the histograms, it is confirmed that the ranges of crystallite sizes are getting reduced with the increasing PVA concentration.
Figure 6.5 HR-SEM images of CoFe$_2$O$_4$ powder synthesized by sol-gel method with different PVA concentration (a) 3 wt% (b) 6 wt% (c) 9 wt% (d) 15 wt%
6.3.5 Magnetic properties

To clarify the magnetic properties of CoFe$_2$O$_4$ powders, the hysteresis loops of the samples prepared by the sol-gel method were measured using VSM. The maximal magnetic field applied in the measurements is 20 kG and the detection was carried out at room temperature. Figure 6.7 shows the magnetisation loops of the samples with various PVA concentrations. Obviously, all the magnetic properties of CoFe$_2$O$_4$ powders show dependence upon the concentration of PVA.
Figure 6.7  Magnetic hysteresis loops measured at room temperature for CoFe$_2$O$_4$ powder synthesized by sol-gel method with different PVA concentration (a) 3 wt% (b) 6 wt% (c) 9 wt% (d) 15 wt%

Figure 6.8 Variation of magnetisation ($M_s$) and retentivity ($M_r$) of CoFe$_2$O$_4$ powder with different PVA amounts added during sol-gel synthesis
As seen from Figure 6.8, the $M_s$ value decreases linearly from 106.6 to 50 Am$^2$/kg as the PVA concentration increases from 3 to 15 wt%. A similar trend is also found in $M_r$, where it reduced from 36.6 to 15.7 Am$^2$/kg with increasing PVA concentration. It is easy to deduce that the evolution behaviours of $M_s$ and $M_r$ are highly dependent on the dispersive growth of CoFe$_2$O$_4$ crystallites. The decrease in $M_s$ may be related to the structural defects, or due to the presence of a relatively non-reactive surface layer that has low magnetisation. It could also be due to the evolution of the average residual strain effects [96].

However, as per Figure 6.9, $H_c$ which is 72.1 kA/m for the sample synthesized with the PVA concentration of 3 wt% decreases to 59.2 kA/m for the sample B, then increases to 67.8 kA/m for the sample C and again decreases to 63 kA/m for the sample synthesized with the PVA concentration of 15wt%. Generally, the coercivity $H_c$ of a magnetic material is a measure of its magneto crystalline anisotropy [97]. It seems to originate from the exchange anisotropy due to spin disorder at the particle interface. This effect is expected to be larger for smaller particles due to the increase in the surface-to volume ratio [98]; however the drastic
decrease and increase in coercivity at 6 and 9 wt% of PVA concentration cannot be attributed only to magneto crystalline anisotropy. As has been reported by other groups [99, 100], $H_c$ is also closely related to the microstructure, particle/grain size, residual strain, domain structure and many other complex factors.

According to the Stoner Wohlfarth model [87], a theoretical value of $M_r/M_s$ is 0.5 for non interacting uniaxial single domain particles, with the easy axis being randomly oriented. The value of the $M_r/M_s$ ratio for all the samples is approximately 0.34 which suggests that all the samples exhibit uniaxial anisotropy. CoFe$_2$O$_4$ crystallites, when used as a recording material should possess reasonable $M_s$, high $H_c$ and low media noise [88]. Taken altogether, these results implied that there existed an optimum PVA concentration (9 wt %), shown in Figure 6.9 as point P, which yielded high $H_c$ and moderate magnetisation $M_s$.

Gharagozlou [56] synthesized cobalt ferrites by polymeric precursor method and studied the influence of calcination temperature on the particle size and magnetic properties. The variation of coercivity reported here, is in agreement with the variation observed by Gharagozlou, where the particle sizes varied from 13 to 135 nm.

Bhame and Joy have reported [101] the synthesis of CoFe$_2$O$_4$ particles of size 900 nm by ceramic method. The $M_s$ and $H_c$ values for the powder samples were 77 Am$^2$/kg and 47.7 kA/m respectively. The present investigation using sol–gel method with PVA 9 wt% concentration provides a moderate magnetisation $M_s$ and a high coercivity $H_c$.

6.4 CONCLUSION

CoFe$_2$O$_4$ ferrites were synthesized by the sol-gel method using PVA as the surfactant in various concentrations. The XRD results confirm the cubic spinel structure of the CoFe$_2$O$_4$ powder. Above 842 °C no endothermic curve was observed in the TG/DSC curve, which corroborates well with the absence of other complex phases in the XRD results. As revealed by the HR-SEM images, increasing the
concentration of PVA breaks up the three dimensional network structure of the products and results in the formation of well dispersed CoFe₂O₄ particles. Significant differences in the magnetic properties were also observed with respect to the PVA concentrations. Though further improvements in \( H_c \) values are still required, these CoFe₂O₄ ferrites synthesized with the PVA concentration of 9 wt% approach to fulfill the requirements of practical recording materials. It demonstrates that the presence of free -OH groups which favour the intra and inter hydrogen bonding within the polymer chains are responsible for the network of polymer matrix and is more effective in size reduction of the ceramic powder.