Chapter-4

Effect of synthesis parameters on the optical properties of α-Fe$_2$O$_3$ thin films
This chapter discusses the optical properties of the $\alpha$-Fe$_2$O$_3$ thin film: optical band gap and refractive index. The effect of different synthesis parameters (NH$_3$ dose, PVA concentration and annealing temperature) on the optical properties of $\alpha$-Fe$_2$O$_3$ thin film is discussed in details. A comparison between the theoretical and experimentally observed values of the band gap is given and an appropriate mechanism for the observed band gap shift is discussed. A description of refractive index variation with the packing density of $\alpha$-Fe$_2$O$_3$ thin film is given in second last section and in last a brief summary of the chapter is given.

4.1 Results and discussion

4.1.1 Variation in optical properties with NH$_3$ dose

The detail of the $\alpha$-Fe$_2$O$_3$ thin film formation is given in chapter 2. For all three sets of experiments, we analyzed morphological and structural changes of the films. We start our discussion with the films formed with the variation of NH$_3$. Fig. 4.1(a) shows the XRD of films formed for 2%, 4% and 6% doses of NH$_3$. The films were investigated using X-ray diffraction (XRD) using Cu K$\alpha$ (1.54 Å) source and the scanning angles from 20° to 65° with step size of 0.02 at room temperature. The XRD shows diffraction peaks corresponding to $\alpha$-Fe$_2$O$_3$ (according to JCPDS-ICCD PDF card No. 33-0664). Crystalline peaks around 32.4° and 35.4° are corresponding to (104) and (110) planes of $\alpha$-Fe$_2$O$_3$ indicating hexagonal (corundum type) structure. The XRD shows that the intensity of crystalline peaks increases with the dose of NH$_3$ which may be due to increasing thickness of $\alpha$-Fe$_2$O$_3$ film as obtained by profilometer data (Table 4.1). The average crystallite size ($D$) in $\alpha$-Fe$_2$O$_3$ films is estimated using Scherrer’s formula [130], $D = 0.9 \lambda/\beta \cos \theta$, where $\beta$ is full width half maximum and $\lambda$ is wavelength of X-rays. The average crystallite size with corresponding lattice parameters is given in Table 4.1.
Figure 4.1: (a) XRD pattern of α-Fe₂O₃ film formed for 2, 4 and 6% doses of NH₃, were annealed at 500 °C. (b), (c) and (d) the SEM images corresponding to 2, 4 and 6% dose of NH₃, respectively.

Table 4.1 Values of dose of NH₃, average thickness (t), crystallite size (D), lattice constant (c/a), optical band gap energy (Eₙ), refractive index (n), and relative density (ρ/ρ₀) for α-Fe₂O₃ films formed at 32 μM PVA concentration.

<table>
<thead>
<tr>
<th>dose of NH₃</th>
<th>t (nm)</th>
<th>D (nm) from XRD</th>
<th>c/a ±0.0002 (Å)</th>
<th>Eₙ±0.01 (eV)</th>
<th>n±0.01 (at 589nm)</th>
<th>ρ/ρ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>75±1.5</td>
<td>14.24±0.81</td>
<td>2.75098</td>
<td>2.72</td>
<td>1.35</td>
<td>0.265±0.011</td>
</tr>
<tr>
<td>4%</td>
<td>155±3.0</td>
<td>15.05±1.01</td>
<td>2.74851</td>
<td>2.56</td>
<td>1.54</td>
<td>0.379±0.013</td>
</tr>
<tr>
<td>6%</td>
<td>400±4.7</td>
<td>16.70±1.30</td>
<td>2.73735</td>
<td>2.53</td>
<td>2.22</td>
<td>0.665±0.014</td>
</tr>
</tbody>
</table>
Figs. 4.1(b) to 4.1(d) show the SEM images of α-Fe₂O₃ films prepared respectively for 2, 4 and 6% doses of NH₃. The increase in thickness of α-Fe₂O₃ film with an increasing dose of NH₃ is due to the presence of large number of NH₃ molecules inside the reaction chamber which react with larger number of precursor ions (Fe³⁺/Fe²⁺) on the solution surface resulting in thicker film. Next, with the increase of thickness of film the crystallite size also increases as the thicker films after annealing contains larger particles [131].

![Graphs showing transmission and optical absorption](image)

**Figure 4.2:** (a) Transmission ($T$) spectra of α-Fe₂O₃ film formed for 2, 4 and 6% doses of NH₃, (b) plot of $(a\nu)^2$ vs $\nu$ of the corresponding α-Fe₂O₃ films.

Coming to the optical properties, the UV-Vis-NIR spectrophotometer was used to observe the variation in the optical band gap and refractive index of α-Fe₂O₃ films. The obtained transmission ($T$) spectra with respect to variation of NH₃ dose are shown in Fig. 4.2(a). There is a decrease in the transmission of α-Fe₂O₃ films with the increase of NH₃ dose. This decrease in transmission is intended due to an increase in crystallite size and thickness of films. From the transmission spectra the optical absorption coefficient ‘$\alpha$’ was calculated using [132], $\alpha = (l/t) \ln (l/l)$, where $t$ is thickness of film. Also, the optical band gap ($E_g$) was calculated using ‘Tauc relation’ [133], $a\nu^2 = C_f(\nu-E_g)^n$, where $C_f$ is a constant, $h$ is Planck’s constant and the prefix $n = 0.5$ for a direct optical band gap transition.

The calculated optical direct band gap values 2.72, 2.56 and 2.53 eV, respectively for 2, 4 and 6% dose of NH₃ (Fig. 4.2(b)) indicate that the optical band gap decreases with the increase of...
films thickness. We know that the variation in optical band gap arises due to: (i) stress induced distortion of optical band gap by film/substrate interactions (ii) density of dislocation (iii) quantum size effect (iv) change in grain boundary barrier height by the change in crystallites size in polycrystalline film [134] and (v) change in lattice symmetry [135]. In our case, as all the films were prepared in similar synthesis conditions on similar substrates so the factors (i) and (ii) may be ignored. The quantum confinement effect is mostly observed in crystallites having size less than 6 nm (for $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ crystallites) [104,136-137]. Next, the grain boundary barrier height depends upon the crystallite size ‘$D$’ according to [138], $E_b = E_{ho} + C(X-fD)^2$, where the original grain boundary barrier height $E_{ho}$, constant $C$, barrier width $X$ and $f$ are specific to the materials. In our case, the variation in the crystallite size is negligible (~14 to 19 nm) so the change in grain boundary barrier height as well would have negligible contribution to the change in band gap.

The lattice modification is reported to affect the electronic level of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ nanocrystals [135]. A decrease in size of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ nanocrystallites is equivalent to an application of a negative pressure, which is expected to lower the lattice symmetry owing to the anisotropic nature of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ lattice and hence the increase in axial ratios $c/a$ as indicated in Table 4.1 [135]. It is noted that size-induced lattice modification ($c/a$) gives the distinct electronic (or magnetic) properties of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ nanocrystals [135]. An increase in $c/a$ ratio results in the increase in ionicity and Fe-O bond separation during the anisotropic expansion of smaller size. The most intense absorption peak of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ [135,139] is given by, $E = -10Dq + 10B + 6C - 26B^2/10Dq$, where $10Dq$ denotes the crystal field splitting, $B$ and $C$ are Racah parameters that describe the neighboring covalency effect in transition metal system [140]. Second-order term ($-26B^2/10Dq$) is extremely small as compared to the sum of $10B$ and $6C$ according to estimated ligand field theory parameters [135]. Since the Racah parameters $B$ and $C$ increase with the reduction of particle size under low pressure [139], the observed blue shift (band gap change) in absorption peak of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ film with the reduction in size is likely the consequence of increase in Racah parameters.

To calculate the refractive index of $\alpha$-$\text{Fe}_{2}\text{O}_{3}$ films the reflectance was determined by using [151], $R = 1 - [T \exp(A)]^{1/2}$, where $A$ is absorption of film. Finally, the refractive index ($n$) of films was calculated using the approximation [140-141], $n = [(I+R)/(I-R)] + [(4R)/(I+R)^2] - (k^2)^{1/2}$, where $k$ is extinction coefficient related to absorption coefficient ($\alpha$) as $k = \alpha l/4\pi$. We observed that at a particular wavelength, the refractive index of film increases with the dose of
NH$_3$ as shown in Fig. 4.3. The observed change in refractive index is due to the change in crystallite size of crystal and film thickness with the dose of NH$_3$ [47]. Also, as the refractive index varies with the packing density of film [142], the increasing crystallite size would increase the packing density and results in an increasing refractive index. The film density has been calculated by using Lorentz–Lorenz relation [143],

$$\rho_f/\rho_b = \frac{\left(\frac{n_f^2 - 1}{n_b^2 + 2}\right)}{\left(\frac{n_f^2 + 2}{n_b^2 - 1}\right)}$$,

where $\rho_f$ is density of $\alpha$-Fe$_2$O$_3$ film, $\rho_b$ is density of bulk $\alpha$-Fe$_2$O$_3$, $n_f$ is refractive index of film and $n_b$ is refractive index of bulk ( $n_b = 3.003$ at $\lambda = 633$ nm) [144]. For $n_f$ values 1.31, 1.47 and 2.01 corresponding to films formed for 2, 4 and 6% dose of NH$_3$, the calculated relative density ($\rho_f/\rho_b$) is given in Table 4.1. These results show that the denser $\alpha$-Fe$_2$O$_3$ films are formed with increasing dose of NH$_3$ which increase the refractive index of film.

![Graph](image)

**Figure 4.3:** Refractive index ($n$) vs wavelength ($\lambda$) plots of $\alpha$-Fe$_2$O$_3$ films formed for 2, 4 and 6% doses of NH$_3$.

### 4.1.2 Variation in optical properties with PVA concentration

The XRD pattern of the films corresponding to the variation of PVA concentration is shown in Fig. 4.4(a). Here the XRD peak intensity decreases with increasing PVA concentration.
This decrease in the peak intensity is due to the decrease in crystalline nature of film by PVA capping effect [145]. Now as calculated from the XRD data (Table 4.2) the crystallite size with respect to PVA concentrations 8, 32 and 80 μM is 26.80, 14.6 and 12.26 nm, respectively. The SEM images from Fig. 4.4(b) to 4.4(d) also show a change in the morphology of films with the concentration of PVA. Fig. 4.4(d) is an aggregation of small nanoparticles which is confirmed by the XRD data and TEM image in Fig 4.4(e).

**Table 4.2.** Value of PVA concentration, average thickness (t), crystallite size (D), lattice constant (c/a), optical band gap energy (Eg), refractive index (n) and relative density (ρ/ρh) for α-Fe₂O₃ films formed at 6% dose of NH₃.

<table>
<thead>
<tr>
<th>PVA (μM)</th>
<th>t (nm)</th>
<th>D (nm) from XRD</th>
<th>c/a ±0.0002 (Å)</th>
<th>Eg ±0.01 (eV)</th>
<th>n ±0.01 (at 589 nm)</th>
<th>ρ/ρh</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>398±2.1</td>
<td>26.80±2.87</td>
<td>2.72088</td>
<td>2.37</td>
<td>2.30</td>
<td>0.685±0.0137</td>
</tr>
<tr>
<td>32</td>
<td>401±1.5</td>
<td>14.6±1.10</td>
<td>2.73747</td>
<td>2.54</td>
<td>2.13</td>
<td>0.663±0.01377</td>
</tr>
<tr>
<td>80</td>
<td>396±2.5</td>
<td>12.26±0.87</td>
<td>2.74502</td>
<td>2.57</td>
<td>2.09</td>
<td>0.532±0.01374</td>
</tr>
</tbody>
</table>

From the TEM image, it is observed that the bigger nanoparticles are aggregation of smaller nanoparticles similar to reported study [146]. So the increasing concentration of PVA results in the reduction of particle size (although they are aggregated).
Figure 4.4: (a) XRD pattern and (b), (c) and (d) the SEM images of $\alpha$-Fe$_2$O$_3$ films formed at 8, 32 and 80 $\mu$M concentration of PVA. (e) the TEM image for 80 $\mu$M concentration of PVA.
When investigated for optical properties, the \( \alpha\text{-Fe}_2\text{O}_3 \) films show increasing transmission with increasing PVA concentration as shown in Fig. 4.5(a). The increasing transmission with PVA concentration is due to the reduction in crystallinity of the particles. The blue shift in transmission spectra (Fig. 4.5(a)) with increasing concentration of PVA shows an increasing optical band gap of \( \alpha\text{-Fe}_2\text{O}_3 \) films. Fig 4.5(b) shows increasing optical band gap 2.37 to 2.54 and then to 2.57 eV corresponding to 8, 32 and 80 \( \mu \text{M} \) concentrations of PVA. Here also the band gap variation can be explained on the basis of change in lattice symmetry as stated in previous case of NH\(_3\). All related parameters are given in Table 4.2.

**Figure 4.5:** (a) shows transmission \( (T) \) spectra of the \( \alpha\text{-Fe}_2\text{O}_3 \) film formed at 8, 32 and 80 \( \mu \text{M} \) concentration of PVA and (b) shows \( (\alpha h \nu)^2 \) vs \( h \nu \) plot of the films.

Now the refractive index decreases in this case with the increasing concentration of PVA as shown in Fig. 4.6 which is again due to the variation in density of \( \alpha\text{-Fe}_2\text{O}_3 \) films. In this case the trend is opposite i.e. the density of film decreases (Table 4.2) with increasing concentration of PVA unlike as with the dose of NH\(_3\) (in case of NH\(_3\)).
The density of films decreases due to the increasing porosity of $\alpha$-Fe$_2$O$_3$ nanoparticles inside the film with increasing concentration of PVA [147]. The PVA molecules being flexible penetrate into the voids between clusters of $\alpha$-Fe$_2$O$_3$ nanoparticles and when the films are annealed the PVA gets evaporated leaving large voids inside the $\alpha$-Fe$_2$O$_3$ particles making them mesoporous. This increase in the porosity (decrease in packing density of $\alpha$-Fe$_2$O$_3$ films) with increasing concentration of PVA results in the decrease of refractive index of films. For application point of view these mesoporous $\alpha$-Fe$_2$O$_3$ nanostructures are highly desirable in many applications e.g. lithium ion battery [148], gas sensors [149], photochemical activity [150] and photo-electrochemical applications [150] etc.

In the above study, we noticed that synthesis parameters i.e. dose of NH$_3$ and PVA concentration have considerable effect on the optical properties of $\alpha$ Fe$_2$O$_3$ films. We also know that annealing temperature is also an important factor for the tuning of the optical properties of
the films [151], so a combined effect of annealing temperature along with these synthesis parameters was also studied in third set of experiment. In this study of annealing temperature, we fixed the dose of NH₃ and concentration PVA and varied only the annealing temperature as discussed in following section.

4.1.3 Variation in optical properties with annealing temperature

To study the effect of annealing temperature, we selected a α-Fe₂O₃ film which was formed at 6% dose of NH₃ and 32 μM concentration of PVA. The α-Fe₂O₃ films were annealed in an argon environment, successively at 200, 400, 600, 800 and 1000 °C temperature. The films were characterized for structural and optical properties as in previous cases. We observed that the films as synthesized and annealed at 200 °C and 400 °C have no peak in XRD. This is probably due to the amorphous nature of films below 400 °C. Fig. 4.7 shows the XRD patterns of films annealed at and above 400 °C.

**Figure 4.7:** XRD patterns of the α-Fe₂O₃ films annealed at 400, 600, 800 and 1000 °C temperature.
Here, only the films annealed above 400 °C have crystalline peak in XRD. Next the crystalline size calculated from the XRD data shows that the film annealed at 600 °C has an average crystallite size of 24±2.1 nm which increased to 31±3.1 nm and then to 46±3.9 nm, respectively for 800 °C and 1000 °C annealing temperature. The variation in particle size of samples annealed at 600, 800 and 1000 °C can also be observed in SEM images in Fig. 4.8.

Figure 4.8: SEM images of α-Fe₂O₃ films annealed at (a) 600 °C, (b) 800 °C and (c) 1000 °C.
Since in XRD no peak was observed, therefore to estimate the particle size inside the films annealed at 200 and 400 °C the corresponding TEM images (Figs. 4.9(a) and 4.9(b)) were processed by Image J software. These samples possesses particle of size about 3±0.5 nm and 6 ±0.78 nm, respectively. The increasing particle size with increasing annealing temperature shows that the crystalline particle size inside the film can be varied by changing either of the parameters i.e. dose of NH₃, concentration of PVA or annealing temperature.

![TEM image](image_url)

**Figure 4.9:** TEM image of annealed α-Fe₂O₃ films (a) at 200 °C and (b) at 400 °C.

Next, Fig. 4.10(a) shows the transmission spectra of these films. With annealing temperature the transmission decreases and a red shift is observed. The decrease in transmission of α-Fe₂O₃ films with increased annealing temperature is due to the increasing in grain size with increasing temperature and increasing roughness due to the formation of big particles which causes increased scattering [152-153].

The optical band gap for these films annealed at 200, 400, 600, 800 and 1000 °C temperature are obtained 2.94, 2.70, 2.58, 2.46 and 2.30 eV, respectively. A maximum band gap 2.94 eV is obtained for the sample annealed at 200 °C which decreases with increasing the annealing temperature as shown in Figs. 4.10(b) and 4.11.
Figure 4.10: (a) the transmission of $\alpha$-Fe$_2$O$_3$ films un-annealed and annealed at 200, 400, 600, 800 and 1000 °C temperature, respectively (b) plot of $(\alpha h\nu)^2$ vs $h\nu$ of $\alpha$-Fe$_2$O$_3$ films.

Here, in this study of varying annealing temperature, we can divide $\alpha$-Fe$_2$O$_3$ films in two categories; one which show quantum size effect as they have smaller crystalline size less than 5 or 6 nm and the others do not show the quantum size effect as they have larger particle size but they show a blue shift due to only the change in lattice symmetry. The particle size dependence of optical band gap due to quantum confinement is given by the following equation [135],

$$E_g = E_g^0 + n^2 h^2 \pi^2 / 2\mu R^2 - 1.8 \varepsilon^2 / \varepsilon R,$$

where $E_g^0$ can be taken as the lowest value of the band gap [136] obtained in our experiment, $R$ is the size of nanoparticle, $\varepsilon$ is the electronic charge, $\varepsilon$ is the dielectric constant and $\mu$ is the effective mass of electron and hole. As we know the smaller particles inside the film show larger optical band gap due to the quantum size effect, therefore we observed a blue shift in 3 nm crystallites film (Fig. 4.12) [136].
Figure 4.11: shows variation of optical band gap ($E_g$) with annealing temperature ($T$).

Figure 4.12 shows that the experimental value of band gap for 3 nm crystallite size coincides with the theoretical value, it indicates that the corresponding film shows the quantum size effect. On increasing the crystalline size above 3 nm with increasing annealing temperature, a deviation between experimental and theoretical values is observed as in Fig 4.12. The observed deviation is inferred due to the partial amorphous nature [154] of $\alpha$-$\text{Fe}_2\text{O}_3$ films as well as the change in lattice symmetry of $\alpha$-$\text{Fe}_2\text{O}_3$ crystallites. The resultant absorption of photons is contributed both by the amorphous and nanocrystalline phase of $\alpha$-$\text{Fe}_2\text{O}_3$ particles and hence the absorption edge in the experimental results show a higher blue shift than theoretical values.
Figure 4.12: plot for optical band gap ($E_g$) vs crystallite size ($D$) for experimental and theoretical values.

Now for second category of $\alpha$-Fe$_2$O$_3$ films which show the variation in band gap with the change in annealing temperature due to the change in lattice symmetry there are other reports as well [110]. In fact, the phase sharing of the octahedran dimer and the electrostatic repulsion of the Fe$^{3+}$ cation are responsible for a trigonal distortion of the octahedran giving rise to C$_{3v}$-type symmetry [155]. Under-sufficient thermal treatment the crystallites inside $\alpha$-Fe$_2$O$_3$ films increase and the structure gets relaxed to maximize the distance between two iron cations in Fe$_2$O$_3$ dimers [110]. As the annealing temperature is increased, the average particle size increases and hence the optical band gap decreases (Fig. 4.13). The variation of particle size inside $\alpha$-Fe$_2$O$_3$ films with annealing temperature is shown in Fig. 4.13(a).
Figure 4.13: (a) plot of particle size \(D\) vs annealing temperature and (b) variation of refractive index \(n\) vs wave length \(\lambda\) of the unheated and annealed \(\alpha\)-Fe\(_2\)O\(_3\) films at different temperature.

Here, the calculated \(c/a\) ratio corresponding to \(\alpha\)-Fe\(_2\)O\(_3\) films annealed at 600, 800 and 1000 °C films are 2.749, 2.739 and 2.732 respectively. As the \(c/a\) ratio decreases with increasing annealing temperature the films show structural relaxation which leads to the decreases in optical band gap.

Finally, the variation in refractive index (1.7 to 2.8 at 589 nm) of these films formed with increasing annealing temperature is shown in Fig. 4.13(b). As expected the \(\alpha\)-Fe\(_2\)O\(_3\) films show an increase in the refractive index with annealing temperature [156-157]. The variation of refractive index with annealing temperature can be correlated with the packing density of the films as in previous cases. Fig. 4.14 shows that the films annealed at lower temperature have lower packing densities than that annealed at higher temperature.
Figure 4.14: Variation of refractive index \((n)\) and relative density \((\rho/\rho_b)\) with annealing temperature \((T)\).

The lower packing density at lower annealing temperature is intended due to the incorporation of oxygen during film growth [144] which creates voids on annealing. As the annealing temperature is increases, the increase in thermal energy facilitates the coalition of small grains which increases the packing density of \(\alpha\)-Fe\(_2\)O\(_3\) films due to reduction of voids [158-159]. As a conclusion in this study we have more room to tune the optical properties of \(\alpha\)-Fe\(_2\)O\(_3\) films since the optical properties can be tailored by varying either one, combination of two or all the process parameters i.e. dose of NH\(_3\), concentration of PVA and annealing temperature.
4.2 Summary

The controlled films of $\alpha$-Fe$_2$O$_3$ have been formed on the surface of precursor solution. Process parameter namely the dose of NH$_3$ easily controls the thickness of floating $\alpha$-Fe$_2$O$_3$ film on the surface of precursor solution and the PVA concentration inside precursor solution controls the size of nanoparticles composing the film. Lattice modification due to the change in lattice symmetry with $\alpha$-Fe$_2$O$_3$ particle size is inferred to be the reason for observed shift in the band gap. Next, the refractive index changes due to the change in the packing density of $\alpha$-Fe$_2$O$_3$ films. The post synthesis annealing temperature tunes the size of resultant crystalline particles which further tunes the optical band gap and refractive index of $\alpha$-Fe$_2$O$_3$ films. Due to the observed significant change in optical band gap without doping, the $\alpha$-Fe$_2$O$_3$ films can be considered for the generation of hydrogen without bias voltage in photocatalytic devices.