CHAPTER 4

SOLID STATE STUDIES
The various solid state studies such as X-ray powder diffraction, IR spectroscopy, thermal analysis, electrical resistivity, magnetic susceptibility, saturation magnetization and electron spin resonance were undertaken. The comparison of different results were made and discussed on the basis of experimental data.

4.1 X-ray diffraction analysis

The formation of monophasic oxides were checked by recording X-ray powder diffractogram of all the samples such as Ce$_{1-x}$Sn$_x$O$_2$, Ce$_{1-x}$Fe$_x$O$_2$, Ce$_{1-x}$Mn$_x$O$_2$ and Sn$_{1-x}$Mn$_x$O$_2$ ($x = 0, 0.1, 0.2, 0.3$ and $1.0$). The d spacing and intensities corresponding to 20 value obtained from the diffractograms were compared with the values reported in the literature (ICDD-PDF files) and found to be in good agreement. Since the d spacing of the intermediate compositions was not reported in the literature, the values were compared with the end members of the series. Figures 4.1-4.4 shows X-ray diffraction pattern of representative samples.

Fig.4.1 shows the XRD pattern of Ce$_{1-x}$Sn$_x$O$_2$ ($x = 0, 0.1, 0.2$ and $0.3$) oxides calcined at $600^\circ$C. Pure CeO$_2$ is in cubic phase and SnO$_2$ is in tetragonal
Figure 4.1 XRD pattern of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ a) $\text{CeO}_2$ b) $\text{Ce}_{0.9}\text{Sn}_{0.1}\text{O}_2$ c) $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ d) $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$
phase. Ce_{0.9}Sn_{0.1}O_2, Ce_{0.8}Sn_{0.2}O_2 and Ce_{0.7}Sn_{0.3}O_2 are in cubic phases and the crystal lattice parameter (5.3857 Å) is smaller than that of calculated pure CeO_2 (5.4189 Å). It may be due to the insertion of Sn atom into the CeO_2 crystal lattice and since the radius of Sn^{4+} (0.81 Å) ion is smaller than that of the Ce^{4+} (0.97 Å), it reduces CeO_2 crystal lattice parameter. On increasing x above 0.3, the XRD diffraction peaks due to CeO_2 become weak and SnO_2 phases are observed. Therefore only small amounts of SnO_2 can be introduced into the CeO_2 lattice to form solid solution and excess SnO_2 remains in a tetragonal phase. The results are in agreement with the literature values. All the X-ray diffraction peaks have been shifted gradually to higher 2θ values with the increase in Sn content in the solid solution which is attributed to the insertion of Sn ions of smaller size into the cubic lattice of CeO_2 resulting in the contraction of it's cell parameter. The XRD pattern of Ce_{0.9}Fe_{0.1}O_2 oxide sintered at 800°C show similar results. Fe_2O_3 has α-hexagonal structure and Ce_{0.9}Fe_{0.1}O_2 is in cubic phase with lattice parameter smaller than that of pure CeO_2. The radius of Fe^{3+} (0.64 Å) ion is smaller than the Ce^{4+} (0.97 Å) ion.

The XRD pattern of Ce_{1-x}Mn_{x}O_2 (x = 0, 0.1, 0.2 and 0.3) is shown in Fig.4.2. The XRD lines of solid solution Ce_{0.9}Mn_{0.1}O_2, Ce_{0.8}Mn_{0.2}O_2 and Ce_{0.7}Mn_{0.3}O_2 are similar to those of CeO_2 indicating the stabilization of the fluorite structure with Mn substitution. On increasing x, diffraction peaks of
Fig. 4.2 XRD pattern of Ce$_{1-x}$Mn$_x$O$_2$ a) CeO$_2$ b) Ce$_{0.9}$Mn$_{0.1}$O$_2$
c) Ce$_{0.8}$Mn$_{0.2}$O$_2$ d) Ce$_{0.7}$Mn$_{0.3}$O$_2$
MnO<sub>2</sub> along with CeO<sub>2</sub> peaks can be seen. All the X-ray diffraction peaks have been shifted gradually to lower 2θ values with the increase in Mn content in the solid solution which is ascribed to the insertion of Mn ions of slightly bigger size into the cubic lattice of CeO<sub>2</sub> resulting in the expansion of it's cell parameter. Accordingly the lattice parameter increases linearly from 5.41°Å to 5.57°Å with increase in Mn content.

Fig.4.3 indicates the XRD pattern of Sn<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>2</sub>. Pure SnO<sub>2</sub> is in tetragonal phase<sup>74</sup>. The solid solution of Sn<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>2</sub>, Sn<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>2</sub> and Sn<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>2</sub> show XRD peaks similar to those of SnO<sub>2</sub> indicating the tetragonal structure. The crystal lattice parameter increases as the Mn content increases due to expansion of the cell parameter. Shift of the CeO<sub>2</sub> pattern towards the lower 2θ values indicates the possible formation of a solid solution<sup>146</sup>.

Fig.4.4 gives X-ray pattern of Copper phthalocyanine. The phthalocyanine compounds exist in different polymorphic forms, the common are α, β and γ- phases and the β form is thermodynamically more stable. The phthalocyanine molecule is a square planar molecule consisting of a divalent metal ion surrounded by four benzopyrrole units. The structure of CuPc is adjudged to be tetragonal with six molecules per unit cell which is in agreement with Robinson and Klein<sup>147</sup>. Well defined diffraction peak in the
Fig. 4.3 XRD pattern of Sn$_{0.9}$Mn$_{0.1}$O$_2$
Fig. 4.4 XRD pattern of Copper phthalocyanine
(001) direction gives the direction of the preferential orientation. The lattice parameter are obtained as \( a = b = 16.68^0 \text{A} \) and \( c = 11.8^0 \text{A} \). Indexing is carried out by comparing the International Centre for Diffraction Data- Powder Diffraction File (ICDD-PDF). The differences in the \( d \) values are attributed to higher X-ray absorption, sample purity, particle size, preferred orientation and crystal texture\(^{147}\). Similar observations were made regarding CoPc, FePc and NiPc. They are having stable \( \beta \)-phase.

4.2 Infra-red spectroscopy

The oxides are characterized by metal-oxygen bonding present in the region from \( 1000 \text{cm}^{-1} - 400 \text{cm}^{-1} \). In the IR spectra of doped compounds, the evolution of new bands can be observed with metal substitution as shown in fig. 4.5-4.9. The frequency of these bands has been related to the strength of metal-oxygen covalency.

In fig. 4.5 in the IR spectra of \( \text{Ce}_{1-x}\text{Sn}_x\text{O}_2 \) (\( x = 0, 0.1, 0.3 \) and 1.0) samples it is observed that as the substitution of \( \text{Sn}^{4+} \) in \( \text{CeO}_2 \) increases, the absorption peak observed at \( 852 \text{ cm}^{-1} \) gets reduced and there is appearance of peaks at \( 620 \) and \( 670 \text{ cm}^{-1} \) which are due to \( \text{Sn-O} \) vibrational modes. These bands are prominent in \( \text{SnO}_2 \) and at slightly lower wave number value at \( 680 \) and \( 610 \text{ cm}^{-1} \) which is in agreement with the literature\(^{39}\). This suggests the
Fig. 4.5 IR spectra of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ a) $\text{CeO}_2$ b) $\text{Ce}_{0.9}\text{Sn}_{0.1}\text{O}_2$ c) $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ d) $\text{SnO}_2$
substitution of Ce$^{4+}$ by Sn$^{4+}$ ions in all the samples. Also there are two small peaks observed at 420 and 450 cm$^{-1}$ of CeO$_2$ stretching vibration in agreement with literature$^{64}$.

In fig. 4.6 in Ce$_{1-x}$Fe$_x$O$_2$ samples, for $x = 0.3$ two sharp absorption peaks at 600 and 652 cm$^{-1}$ are seen. Also peak at 852 cm$^{-1}$ is reduced which is of Ce-O stretching vibrational mode. The two bands are shifted at 546 and 450 cm$^{-1}$ and they are sharp and of strong intensity in $\alpha$-Fe$_2$O$_3$$^{149}$.

Fig.4.7 shows the IR spectra of Ce$_{1-x}$Mn$_x$O$_2$ series. It is observed that as the x increases the Ce-O band at 852 cm$^{-1}$ gets reduced and there are appearance of bands at 510 and 580 cm$^{-1}$ due to Mn–O vibrations. These bands are of strong intensity in Ce$_{0.7}$Mn$_{0.3}$O$_2$ than MnO$_2$. Fig.4.8 shows the IR spectra of Sn$_{1-x}$Mn$_x$O$_2$ samples. Evolution of Mn-O band at 510 cm$^{-1}$ can be seen with the increase of x in Sn$_{1-x}$Mn$_x$O$_2$ composition. The absorption peak at 680 cm$^{-1}$ disappears gradually, showing substitution of Sn$^{4+}$ by Mn$^{4+}$ ions.

Phthalocyanines are characterized by IR Spectroscopy$^{82,108,111-112}$. IR spectra of metal phthalocyanines are shown in fig.4.9. IR spectra show following absorption peaks. The peaks around 1121-1123, 1090-1092, 1067-1070, 947-949, 872-885 and 754 cm$^{-1}$ are due to phthalocyanine skeletal vibrations. The peaks observed at 1420 – 1423 and 1335 cm$^{-1}$ is due to aromatic phenyl ring. The peaks around 1286, 1226 and 1202 -1210 cm$^{-1}$ are
Fig. 4.6 IR spectra of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ a) $\text{SnO}_2$ b) $\text{Ce}_{0.7}\text{Fe}_{0.3}\text{O}_2$ c) $\alpha$-Fe$_2$O$_3$
Fig. 4.7 IR spectra of $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ a) $\text{Ce}_{0.7}\text{Mn}_{0.3}\text{O}_2$ b) $\text{MnO}_2$
Fig. 4.8 IR spectra of $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$ a) $\text{Sn}_{0.8}\text{Mn}_{0.2}\text{O}_2$, b) $\text{Sn}_{0.7}\text{Mn}_{0.3}\text{O}_2$ c) $\text{MnO}_2$
Fig. 4.9 IR spectra of metal phthalocyanines a) CuPc b) CoPc c) FePc d) NiPc
due to C-N stretch. The peaks assigned to C-H in plane bending around 1165-
67, 1001-1005 cm\(^{-1}\) and peaks due to C-N bending at 901 cm\(^{-1}\) and 799 - 802
\(\text{cm}^{-1}\) respectively. The peaks at 770 - 773 cm\(^{-1}\) are due to C-H out of plane
bending. Broad peak at 3400 -3415 cm\(^{-1}\) is attributed to the hydrogen bonding
formed between the nitrogen atom of the Pc macromolecule and H atom of the
moisture absorbed on the KBr pellets. The sharp peaks observed at 1610 -
1616 cm\(^{-1}\) are attributed to C = C, C = N and ring stretching (skeletal band).

4.3 Thermal Analysis

Co-precipitated hydroxide precursors before decomposition were
subjected to thermal analysis studies, to find out the decomposition
temperature of hydroxides and then the initiation of solid- state diffusion
reaction. Metal phthalocyanines were subjected to thermal treatment to check
the thermal stability of the phthalocyanines. TG/DSC pattern of representative
samples are shown in figures 4.10 – 4.13.

Thermo-gravimetric studies show three major steps in the decomposition
process and the probable reactions are

1. Dehydration

2. Decomposition of hydroxides to corresponding oxides and followed by
3. Solid-state diffusion reaction leading to solid solution formation in mixed oxides.

The reactions taking place during heating in the case of mixed oxides may be represented by following steps:

\[
\begin{align*}
M(OH)_{n\times xH_2O} + M'(OH)_{n\times xH_2O} \rightarrow M(OH)_n + M'(OH)_n + 2xH_2O \\
M(OH)_n + M'(OH)_n \rightarrow MO_n + M'O_n + xH_2O \\
MO_n + M'O_n \rightarrow MM'O_n
\end{align*}
\]

Where \( M \) and \( M' \) are metal ions and \( n \) indicate the number depending on oxidation state of the metal.

Figure 4.10 show TG/DSC pattern of cerium tin co-precipitated hydroxide decomposition. First weight loss is around 100°C for the elimination of water. Further weight loss is around 150-350°C due to decomposition of hydroxide and on further heating leads to the solid solution. There are two endothermic DSC peaks at 92 and 308°C respectively corresponding to two weight losses. These results are in accordance with literature. Since solid-state diffusion being slow process and takes place over a range of temperatures, no sharp change in thermal event is observed.

Fig. 4.11 shows a weight loss for \( \text{Ce}_{0.9}\text{Fe}_{0.1}(\text{OH})_4 \) precursor decomposition between 90-120°C due to the loss of moisture and further weight loss between 250-300°C due to decomposition of hydroxides and
Fig. 4.10 TG/DSC pattern of Ce$_{0.8}$Sn$_{0.2}$(OH)$_n$.xH$_2$O precursor decomposition
Fig. 4.11 TG/DSC pattern of Ce$_{0.9}$Fe$_{0.1}$(OH)$_n$.xH$_2$O precursor decomposition
initiation of solid state diffusion leading to oxide formation. Two endothermic DSC peaks are observed at 118°C and 263°C corresponding to elimination of water and hydroxide decomposition.

In the fig. 4.12 TG/DSC pattern of SnMn(OH)$_4$·$x$H$_2$O precursor decomposition, weight loss is observed between 90-120°C due to the loss of water and further weight loss around 250-300°C due to decomposition of hydroxides and after that initiation of a solid state diffusion up to 800°C leading to solid solution formation. The Ce-Mn hydroxide decomposition shows similar TG/DSC pattern.

Fig.4.13 depicts the TG/DSC pattern of CoPc decomposition. It starts decomposing at 425°C and shows weight loss till 700°C. An exothermic peak is seen at 484°C. The decomposition products suspected to be formed are phthalic residue, ammonia and cobalt oxide. At 745°C there is sharp endothermic rise due to the formation of metal oxide as indicated by DSC peak$^{151}$. Copper phthalocyanine does not have sharp melting point$^{42}$. It starts decomposing at 450°C and shows weight loss till 800°C. An exothermic peak around 459°C corresponds to CuPc decomposition. At 830°C there is sharp endothermic rise may be due to the formation of CuO as indicated by DSC peak.
Fig. 4.12 TG/DSC pattern of Sn$_{0.9}$Mn$_{0.1}$(OH)$_n$.xH$_2$O precursor decomposition
Fig 4.13 TG/DSC pattern of CoPc decomposition
The TG/DSC patterns of NiPc and FePc are slightly different than that of CoPc and CuPc. They start decomposing around 200-300°C.

The thermal stability of the phthalocyanine molecule is due to its extremely high aromatic character which exceeds that of a benzene ring by a factor of 15\(^8\). The thermal stabilities of the substituted phthalocyanines are lower than those the unsubstituted, FePc or CoPc compounds

**4.4 Electrical resistivity**

Electrical resistivity of the prepared samples were measured using two probe method at various temperature range from room temperature to 250\(^0\)C. The resistivity of these oxides was found in the semiconducting range. Plot of resistivity log \((\rho)\) versus inverse temperature are shown in figures 4.14 - 4.18. The resistivity of the phthalocyanines was measured from room temperature to 150\(^0\)C. Resistivity was found to decrease with increase in the temperature for all the compositions under investigation.

Fig 4.14 shows the resistivity behaviour of Ce\(_{1-x}\)Fe\(_x\)O\(_2\) series during cooling cycles. Pure Cerium oxide is basically a poor oxide ion conductor. When trivalent dopant cations \((M^{3+})\) substitute for Ce\(^{4+}\), one oxygen- ion is introduced for every second M\(^{3+}\) cation. The conductivities are significantly enhanced in Ce\(_{1-x}\)Fe\(_x\)O\(_2\) solids by increasing the oxygen vacancies \((V_0^-)\) \(^{36}\). The
Fig. 4.14 Variation of electrical resistivity of Ce$_{1-x}$Fe$_x$O$_2$ with temperature
electrical resistivity decreases systematically with increasing Fe substitution and reaches a maximum for the composition Ce$_{0.7}$Fe$_{0.3}$O$_2$.

For Ce$_{1-x}$Sn$_x$O$_2$ series as shown in Fig. 4.15 all the samples show linear decrease in resistivity showing semiconducting behaviour. Resistivity value is highest for Ce$_{0.8}$Sn$_{0.2}$O$_2$. SnO$_2$ is an n-type semiconductor since oxygen vacancies or interstitial Sn$^{4+}$ are donor sites$^{48,98}$. According to literature$^{39}$ for CeO$_2$-SnO$_2$ samples the variation of log $\rho$ Vs 1000/T show two different slopes, which may be assigned to two different conduction mechanisms, due to the migration of charge carriers in presence of pores. The sample lose water on dry argon flushing, indicating contribution of protonic conduction on wet samples. The progressing dehydration is accompanied by the decrease of conductivity. The conductivity of SnO$_2$ increases with increasing reduction or non-stoichiometry of the oxide. Doped SnO$_2$ are characterized by high electrical conductivity. A plot of log $\rho$ Vs 1000/T for Sn$_{1-x}$Mn$_x$O$_2$ series is shown in fig.4.16.

Similar observation can be made for Ce$_{1-x}$Mn$_x$O$_2$ series as shown in fig.4.17. The resistivity decreases with increase in temperature i.e. conductivity increases with temperature showing semiconducting behaviour.

Phthalocyanines are a class of organic semiconductors, whose electrical properties have considerable importance owing to their potential application in
Fig. 4.15 Variation of electrical resistivity of Ce$_{1-x}$Sn$_x$O$_2$ with temperature
Fig. 4.16 Variation of electrical resistivity of $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$ with temperature
Fig. 4.17 Variation of electrical resistivity of Ce$_{1-x}$Mn$_x$O$_2$ with temperature
electronic devices and sensor systems. Achar and Lokesh\textsuperscript{106} studied the electrical conductivity measurement for freshly prepared four polymorphs of CuPc in the temperature range 25-200\textdegree{}C in the air atmosphere and found a marked difference in variation of electrical properties with temperature for different phases before and after the heat treatment. A phthalocyanine molecule is a good electron donor. The ring of N- atoms around the central metal atoms forms a potential well which is responsible for the semiconducting properties. Transfer of charge between molecules in films or single crystal is only possible by crossing the potential well\textsuperscript{8}.

Electrical resistivities of the phthalocyanines were studied from room temperature to 150\textdegree{}C. They showed decrease in resistivity with temperature. Resistivity pattern of the phthalocyanines is shown in fig.4.18.

4.5 Magnetic susceptibility

The magnetic susceptibility of different paramagnetic samples was determined by Gouy method at room temperature using field strength of 8000 gauss. The magnetic moments in Bohr Magneton were calculated using an expression

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_m \times T},$$

Where, $\chi_m$ is the molar susceptibility at room temperature, $T$ is the temperature.
Fig. 4.18 Variation of electrical resistivity of metal phthalocyanines with temperature
The observed gram susceptibility of oxides is shown in table 4.1-4.3. Most of the samples are paramagnetic. The magnetic susceptibility values of Ce$_{1-x}$Fe$_x$O$_2$ were in the range of $2.984 \times 10^{-6}$ to $14.37 \times 10^{-6}$ cgs units. For Ce$_{1-x}$Sn$_x$O$_2$ series, the values were $7.64 \times 10^{-6}$ to $2.68 \times 10^{-6}$ cgs units decreasing with Sn substitution and for Ce$_{1-x}$Mn$_x$O$_2$ series, the values were in the range of $4.06 \times 10^{-6}$ to $6.84 \times 10^{-6}$ cgs units increasing with the Mn substitution. The magnetic moment also increases which comes from both Mn$^{4+}$ and Ce$^{3+}$ ions. For Sn$_{1-x}$Mn$_x$O$_2$ series, the values were $5.16 \times 10^{-6}$ to $18.60 \times 10^{-6}$ cgs units increasing with Mn substitution. The diamagnetic nature gradually changes to paramagnetic nature with Mn substitution in SnO$_2$ doped samples.

Among phthalocyanines, Cobalt phthalocyanine and Copper phthalocyanine are paramagnetic in nature. Achar and Lokesh$^{106}$ studied the magnetic susceptibility of $\alpha$, $\beta$, $\gamma$ and $\delta$ Copper phthalocyanine polymorphs at ambient temperature and varying the magnetic field strengths. They found that higher or lower values of $\mu_{\text{eff}}$ indicate the contribution of direct or super exchange intermolecular interaction spacing and inclination of the molecules in the crystal lattice. During the process of stacking, each Pc molecule is stacked to the neighboring molecule along the b-axis in such a way that each molecule is contributing either a nitrogen atom at inter-planar distance of $3.38^\circ A$ above or below the central metal. This inter-planar distance provide a suitable
Table 4.1 The Magnetic susceptibility values of Ce$_{1-x}$Fe$_x$O$_2$ and Ce$_{1-x}$Sn$_x$O$_2$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic susceptibility ($\chi_\varepsilon$ cgs units)</th>
<th>$\mu_{\text{eff}}$ (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>2.984 x 10$^{-6}$</td>
<td>1.06</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Fe$</em>{0.1}$O$_2$</td>
<td>8.987 x 10$^{-6}$</td>
<td>1.80</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Fe$</em>{0.2}$O$_2$</td>
<td>11.2 x 10$^{-6}$</td>
<td>1.95</td>
</tr>
<tr>
<td>Ce$<em>{0.7}$Fe$</em>{0.3}$O$_2$</td>
<td>14.37 x 10$^{-6}$</td>
<td>2.14</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Sn$</em>{0.1}$O$_2$</td>
<td>7.39 x 10$^{-6}$</td>
<td>1.66</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Sn$</em>{0.2}$O$_2$</td>
<td>7.20 x 10$^{-6}$</td>
<td>1.63</td>
</tr>
<tr>
<td>Ce$<em>{0.7}$Sn$</em>{0.3}$O$_2$</td>
<td>2.68 x 10$^{-6}$</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 4.2 The Magnetic susceptibility values of Ce$_{1-x}$Mn$_x$O$_2$ and Sn$_{1-x}$Mn$_x$O$_2$ series

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic susceptibility ($\chi_e$ cgs units)</th>
<th>$\mu_{\text{eff}}$(BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.9}$Mn$</em>{0.1}$O$_2$</td>
<td>$4.06 \times 10^{-6}$</td>
<td>1.21</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Mn$</em>{0.2}$O$_2$</td>
<td>$4.98 \times 10^{-6}$</td>
<td>1.30</td>
</tr>
<tr>
<td>Ce$<em>{0.7}$Mn$</em>{0.3}$O$_2$</td>
<td>$6.84 \times 10^{-6}$</td>
<td>1.48</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>$84.98 \times 10^{-6}$</td>
<td>3.84</td>
</tr>
<tr>
<td>Sn$<em>{0.9}$Mn$</em>{0.1}$O$_2$</td>
<td>$5.165 \times 10^{-6}$</td>
<td>1.27</td>
</tr>
<tr>
<td>Sn$<em>{0.8}$Mn$</em>{0.2}$O$_2$</td>
<td>$9.2 \times 10^{-6}$</td>
<td>1.66</td>
</tr>
<tr>
<td>Sn$<em>{0.7}$Mn$</em>{0.3}$O$_2$</td>
<td>$18.6 \times 10^{-6}$</td>
<td>2.17</td>
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</tbody>
</table>
Table 4.3 The Magnetic susceptibility values of Metal phthalocyanines

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic susceptibility</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper phthalocyanine</td>
<td>$27.9 \times 10^{-6}$</td>
<td>2.61</td>
</tr>
<tr>
<td>Cobalt phthalocyanine</td>
<td>$1.8 \times 10^{-6}$</td>
<td>1.58</td>
</tr>
</tbody>
</table>
pathway for spin-spin coupling interaction between adjacent metal atoms either directly or super exchange through the N atoms of the molecule.

4.6 Saturation magnetization

The saturation magnetization was measured for the magnetic samples such as $\alpha$-Fe$_2$O$_3$ and FePc using hysteresis loop tracer. The results are shown in table 4.4. Since the magnetic susceptibility values are higher, magnetic moments were calculated for these samples using Nickel as a standard material.

4.7. ESR Study

ESR studies were carried out for various samples to get an insight about the photo-catalytically active and paramagnetic species. The technique was used as qualitative tool to ascertain the changes occurring with doping in CeO$_2$ structure. ESR data of representative samples recorded at room temperature is presented in table 4.5. ESR spectra of some representative samples are shown in figures 4.19 a-c. The line width depends on the relaxation time of the spin state through either or both of the processes. (1) spin-lattice relaxation and (2) spin-spin relaxation. The interaction of the paramagnetic ions with the thermal vibrations of the lattice leads to a short spin-lattice relaxation time.
Table 4.4 The observed Saturation magnetization values at room temperature

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Saturation magnetization emu/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni (standard))</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>3.18</td>
</tr>
<tr>
<td>3</td>
<td>Iron phthalocyanine</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Table 4.5 ESR data of representative samples at room temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>g value</th>
<th>Line width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{\textgreek{c}})</td>
<td>(\text{gauss})</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>3.8598</td>
<td>384</td>
</tr>
<tr>
<td></td>
<td>4.4974</td>
<td>192</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Fe$</em>{0.2}$O$_2$</td>
<td>2.0080</td>
<td>672</td>
</tr>
<tr>
<td></td>
<td>4.302</td>
<td>640</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Mn$</em>{0.1}$O$_2$</td>
<td>2.0041</td>
<td>400</td>
</tr>
<tr>
<td>Sn$<em>{0.9}$Mn$</em>{0.1}$O$_2$</td>
<td>1.962</td>
<td>1680</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Sn$</em>{0.2}$O$_2$</td>
<td>4.5033</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>2.0673</td>
<td>112</td>
</tr>
<tr>
<td>CuPc</td>
<td>2.00277</td>
<td>500</td>
</tr>
<tr>
<td>CoPc</td>
<td>2.5962</td>
<td>1912</td>
</tr>
</tbody>
</table>
ESR signal in CeO$_2$ is due to paramagnetic Ce$^{3+}$ anion vacancy$^{17,35}$. The ESR spectrum of CeO$_2$ shows peaks at $g = 3.85$ and $g = 4.49$ due to Ce$^{3+}$ type defects present in CeO$_2$ crystalline structure$^{19}$. There is no ESR signal due to Ce-Mn because Mn$^{3+}$ and Mn$^{4+}$ are ESR inactive.

ESR spectra of copper phthalocyanine and cobalt phthalocyanine are presented in fig.4.19. The data are in agreement with the magnetic susceptibility measurement regarding the paramagnetic nature of the compounds. The ESR signal observed is due to $-1/2 \, g\beta H$ to $+1/2 \, g\beta H$ transition, where $g$ is the Lande, or spectroscopies splitting factor, $\beta$ is the electron Bohr magneton and $H$ is the applied magnetic field. This single energy transition signal is modified with the axially symmetric copper phthalocyanine which has D$_{4h}$ symmetry$^{106}$.

In an ideal case for CuPc, the unpaired copper d$_{x^2-y^2}$ electron residing in D$_{4h}$ symmetry interacts with its own nucleus of spin 3/2 and each of its four ligands nitrogen nuclei of spin 1. So, 36 discrete transition signals with the intensity ratio 1:4:10:16:19:16:10:4:1 for each of 4 subsets are expected. But all the ESR signals of copper phthalocyanine showed with partial resolution and overlapping of the hyperfine structure due to copper atom and superfine structures due to the 4 nitrogen atoms$^{106}$. 


Fig. 4.19 b) shows ESR spectra of Ce$_{0.8}$Fe$_{0.2}$O$_2$ sample recorded at room temperature. The spectrum shows a broad line with two low intensity peaks at g values of about 2.0 and 4.3. Fe$^{3+}$ has five unpaired electrons in the low field, high spin state ($^6S_{5/2}$) and only one in high field. In the former case, since the symmetry is spherical, g = 2.0080. Only one signal at the same g value would be observed in perfect tetrahedral or octahedral symmetries. In distorted tetrahedral or distorted octahedral symmetries the powder spectrum can display signals with g from 2 to 6 when the symmetry is lower than D$_{4h}$ (orthorhombic) one can observe an isotropic signal in the range g = 4.29.

In the present study, the g = 2.0080 in Ce$_{0.8}$Fe$_{0.2}$O$_2$ sample is assigned to Fe$^{3+}$ ions incorporated in the ceria lattice.
Fig. 4.19 ESR spectra of a) CuPc b) Ce$_{0.8}$Fe$_{0.2}$O$_2$ c) CoPc