CHAPTER – III

Characterization of rubidium and cesium ferrites (MFeO$_2$) prepared by solution combustion and precursor methods:

3.1 Introduction:

Alkali metal ferrites are the ferrimagnetic oxide materials exhibiting high magnetization, Curie temperature, resistivity/permeability and low eddy current losses. These materials are extensively used in high capacity batteries, intercalation electrodes in rechargeable batteries, strong oxidizing agents, audio-video digital recording and low magnetization ferrofluids [1-4]. Alkali metal ferrite synthesis has gained significant attention due to its wide range of applications in high density storage devices, microwave devices, humidity sensors, DNA separation, magnetic resonance imaging (MRI) and hyperthermia [5-9]. Recently, there has been a surge of interest in the preparation of nanosized alkali metal ferrites as their properties are quite different from bulk of the material of the same composition [10, 11]. The synthesis of nanoparticles with controlled size, shape and composition is of fundamental and technological interest and will have important consequences in many fields of nanotechnology [12]. Hence, the methodology aspect has become the most important factor in the design and preparation of ferrite materials. The most extensively used technique for the bulk preparation of ferrites is the conventional ceramic method. However, this method has certain limitations viz. milling of the starting materials which incorporates lattice defects and strains in the ferrite obtained which, in turn, affect its permanent magnetic properties. The milling process may also cause loss of sample due to adhesion of sample to grinding surfaces. This can lead to possible changes in the stoichiometry of the desired products. Furthermore, during traditional solid state mixing or milling, contamination or introduction of impurities to the sample from grinding surfaces may be unavoidable. Solid state reactions require high temperature heat treatment which can cause evaporation of some of the constituent metal oxides or phase changes e.g. Fe$_3$O$_4$ to Fe$_2$O$_3$ [13]. This can result in the final products having modified stoichiometric composition or samples with unreproducible characteristics. Finally, it involves sintering at high temperature for a long time resulting in particle coarsening and aggregation i.e. loss of the fine particle nature [14-18]. Also, this method is intrinsically slow because although the reactant oxides are well mixed at the level of individual particles, on the atomic scale they are very inhomogeneous. On the other hand, the
The last three decades have witnessed a phenomenal progress in the field of thermal analysis especially in instrumentation and widening scope of its applications. The applications of thermal techniques encompass a wide spectrum of field ranging from pure to applied science and technology. It contributes significantly to evolution of large variety of high tech materials used in specialized area of industry. Thermal techniques in combination with other physico-chemical tools such as Mössbauer, IR and XRD provide very useful information to get insight into the mechanism of solid-state decomposition of ferricarboxylates leading to the formation of ferrite materials [19-22]. The metal ferricarboxylate complexes have proven to be the most suitable precursors owing to their better complexing ability, ease to decomposition and change of oxidation state etc. In the present chapter, we report the synthesis of pure rubidium and cesium ferrites with formula MFeO$_2$ by solution combustion method. For the sake of comparison, the same ferrites have also been prepared by precursor method involving thermal decomposition of metal ferricarboxylate (M$_3$[Fe(L)$_6$].xH$_2$O) (L= formate, acetate, propionate, butyrate, oxalate and citrate) precursors.
3.2 Results and discussion

3.2.1 Studies on rubidium and cesium ferrite prepared by solution combustion method

3.2.1.1 Characterization of rubidium and cesium ferrites:

The ferrite, MFeO$_2$ (M=Rb, Cs) obtained from the solution phase combustion of respective metal nitrate, ferric nitrate and capping agent (ODH/urea). Oxalyl dihydrazide/urea acts as fuel for the reaction.

\[
\begin{align*}
600^\circ C & \quad \text{MNO}_3(aq) + \text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}(aq) + 2 \text{C}_2\text{H}_6\text{N}_4\text{O}_2(aq) \rightarrow \text{MFeO}_2 + 4\text{CO}_2(g) \\
& \quad (M=Rb,Cs) \quad \text{(ODH)} \quad + 6\text{N}_2 (g) + 15\text{H}_2\text{O}(g)
\end{align*}
\]

\[
\begin{align*}
600^\circ C & \quad \text{MNO}_3(aq) + \text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}(aq) + 2 \text{NH}_2\text{-CO-NH}_2(aq) \rightarrow \text{MFeO}_2 + 4\text{CO}_2(g) \\
& \quad (M=Rb,Cs) \quad \text{(urea)} \quad + 2\text{N}_2 (g) + 15\text{H}_2\text{O}(g)
\end{align*}
\]

The final product has been characterized by different physico-chemical techniques. XRD powder pattern (Figure 1) of the RbFeO$_2$ ferrite obtained resembles to that of cubic ferrite (α-LiFeO$_2$) already reported [23]. Mössbauer spectrum of the ferrite obtained (Figure 2) exhibits a symmetrical doublet with isomer shift and quadrupole splitting values of 0.19 and 0.64 mms$^{-1}$ respectively. These parameters correspond to Fe$^{3+}$ ions in tetrahedral coordination and are in agreement with already reported for analogous cesium ferrites respectively [24-26]. TEM analysis (Figure 3) reveals that the average particle size of the ferrite obtained is 30 nm.

The cesium ferrite, CsFeO$_2$ prepared by employing solution phase combustion method has been characterized by Mössbauer spectrum (Figure 4) which exhibits a doublet with isomer shift and quadrupole splitting values of 0.32 and 0.72 mms$^{-1}$ respectively. These parameters are in agreement with those reported in literature [24-26]. XRD powder pattern (Figure 5) of the final thermolysis residue also reveals the existence of CsFeO$_2$ with CsAlO$_2$ type geometry [27]. TEM analysis (Figure 6) shows that the average particle size of the ferrite obtained is 35 nm.
3.2.2 Characterization of rubidium ferrite obtained from rubidium ferrimonocarboxylate precursors (Precursor method):

Infra-red (IR) spectrum of rubidium hexa(formato)ferrate(III) trihydrate precursor shows a broad band centered at about 3270 cm\(^{-1}\) due to \(\nu(\text{O-H})\) of lattice water and a distinct shoulder at 2870 cm\(^{-1}\) due to \(\nu(\text{C-H})\) of the formate group. Intense bands in the ranges 1625-1660 cm\(^{-1}\) and 1370-1410 cm\(^{-1}\) are attributed to \(\nu_{\text{asy}}(\text{C=O})\) and \(\nu_{\text{sym}}(\text{C=O})\) of the coordinated formate groups [28]. A small but distinct band at 580 cm\(^{-1}\) due to \(\nu(\text{Fe-O})\) suggests the presence of Fe-O (carboxylate) bonding [29]. The other precursors (acetate, propionate and butyrate) display almost similar IR spectra. However, the anhydrous precursors (propionate and butyrate) do not show the presence of \(\nu(\text{O-H})\) of lattice water.

Mössbauer spectra of the rubidium ferrimonocarboxylate precursors exhibit a doublet (Figure 7) with isomer shift (\(\delta\)) and quadrupole splitting (\(\Delta\)) values within the range 0.31-0.38\(\pm\)0.004 mms\(^{-1}\) and 0.35-0.40\(\pm\)0.005 mms\(^{-1}\) respectively. These parameters correspond to those reported for high spin ferric ions in octahedral coordination [30]. The asymmetry in the intensity of quadrupole lines may be attributed to the prefential orientation, a phenomenon common in polycrystalline iron materials. The coordination number of six for iron is satisfied by six formate ligands which bind to iron through oxygen atoms of the carboxylate groups.

3.2.2.1 Thermal decomposition studies

The compoundwise discussion on the thermal decomposition of various rubidium hexa(monocarboxylato)ferrate(III) precursors follows:

3.2.2.1.1 Rubidium hexa(formato)ferrate(III) trihydrate, Rb\(_3\)[Fe(HCOO)\(_6\)]. 3H\(_2\)O

Figure 8 shows the simultaneous TG-DTG-DTA curves of rubidium hexa(formato)ferrate(III) trihydrate in flowing air atmosphere at a heating rate of 10\(^0\)C min\(^{-1}\). The precursor undergoes dehydration till a mass loss of 8.5% is reached at 106\(^0\)C (cal. loss = 8.48%). The corresponding broad DTA (endotherm) and DTG peaks are centered at about 69\(^0\)C and 63\(^0\)C respectively. The anhydrous precursor is not stable as shown by the absence of an arrest in TG and immediately undergoes an exothermic decomposition to yield rubidium carbonate and Fe\(_2\)O\(_3\) with a mass loss of 32.6% at 380\(^0\)C (cal. loss = 33%).
Fig. 1: XRD powder pattern of RbFeO$_2$ prepared by combustion method.

Fig. 2: Mössbauer spectrum of RbFeO$_2$ prepared by combustion method.
Fig. 3: TEM Micrograph of RbFeO$_2$ prepared by combustion method.

Fig. 4: Mössbauer spectrum of CsFeO$_2$ prepared by combustion method.
Fig. 5: XRD powder pattern of CsFeO$_2$ prepared by combustion method.

Fig. 6: Transmission Electron Micrograph of CsFeO$_2$ prepared by combustion method.
Corresponding to this step, DTA shows an exotherm at 245\(^{\circ}\)C while DTG displays a respective distinct signal at 250\(^{\circ}\)C. The presence of Fe\(_2\)O\(_3\) has been confirmed by recording the Mössbauer spectrum (Figure 9) of the residue obtained by calcining the precursor isothermally at 380\(^{\circ}\)C for 15 min. The spectrum exhibits a symmetrical six line pattern with isomer shift and internal magnetic field values of 0.39 mm/s and 51.4 Tesla respectively (Table 1). These parameters are in close agreement to those reported [31, 32] for \(\alpha\)-Fe\(_2\)O\(_3\) of bulk size. The existence of Rb\(_2\)CO\(_3\) has been affirmed by recording the IR spectrum of the residue that displayed a characteristic carbonate peak at 1430 cm\(^{-1}\). After remaining stable up to 850\(^{\circ}\)C, rubidium carbonate decomposes into rubidium oxide with the evolution of CO\(_2\) as indicated by the presence of an endotherm at 870\(^{\circ}\)C. Finally, rubidium oxide and \(\alpha\)-Fe\(_2\)O\(_3\) undergo solid-state reaction above 900\(^{\circ}\)C as reflected by an exotherm to yield rubidium ferrite, RbFeO\(_2\) accompanied by a mass loss of 56.4% (cal. loss= 56.7%). XRD powder pattern of the final thermolysis residue (Figure 10) shows the existence of two phases i.e. RbFeO\(_2\) and Rb\(_2\)O. The
identity of the ferrite as RbFeO\(_2\) has also been confirmed by recording Mössbauer spectrum (Figure 11) of the ultimate residue that displays a doublet with isomer shift (\(\delta\)) and quadrupole splitting (\(\Delta\)) values of 0.37 mms\(^{-1}\) and 0.69 mms\(^{-1}\) respectively. These parameters are in agreement to those reported [24-26] for analogous cesium ferrite (CsFeO\(_2\)). In order to get pure ferrite i.e. RbFeO\(_2\), the unreacted Rb\(_2\)O was removed from the final thermolysis residue by treating it with conc. HNO\(_3\). TEM micrograph (Figure 12) shows spherical morphology of particles with strong agglomeration due to magnetic interaction of the particles. The average particle size of RbFeO\(_2\) obtained is 45 nm.

Based on the above discussion, the following pathway for the thermal decomposition of rubidium hexa(formato)ferrate(III) trihydrate precursor is proposed:

\[
\begin{align*}
\text{Rb}_3[\text{Fe(HCOO)}_6].3\text{H}_2\text{O} & \xrightarrow{106^0\text{C}} \text{Rb}_3[\text{Fe(HCOO)}_6] + 3\text{H}_2\text{O}(g) \\
\text{dehydration} \\
\text{Rb}_3[\text{Fe(HCOO)}_6] & \xrightarrow{380^0\text{C}} \frac{3}{2}\text{Rb}_2\text{CO}_3 + \frac{1}{2}\text{Fe}_2\text{O}_3 + \text{gaseous products} \\
\text{exo-decomp.} \\
\frac{3}{2}\text{Rb}_2\text{CO}_3 & \xrightarrow{880^0\text{C}} \frac{3}{2}\text{Rb}_2\text{O} + \frac{3}{2}\text{CO}_2 \\
\text{end-decomp.} \\
\frac{1}{2}\text{Rb}_2\text{O} + \frac{1}{2}\text{Fe}_2\text{O}_3 & \xrightarrow{>900^0\text{C}} \text{RbFeO}_2
\end{align*}
\]

3.2.2.1.2 Rubidium hexa(acetato)ferrate(III) monohydrate, Rb\(_3\)[Fe(CH\(_3\)COO)\(_6\)].H\(_2\)O
Figure 13 presents the simultaneous TG-DTG-DTA curves of rubidium hexa(acetato)ferrate(III) monohydrate at a heating rate of 10°C min⁻¹. Dehydration of the precursor commences at 60°C and completes at 103°C as indicated by a mass loss of 2.9%. The corresponding broad DTA (endotherm) and DTG peaks are centered at 72°C and 65°C respectively. Anhydrous rubidium ferriacetate then undergoes exothermic decomposition to yield rubidium acetate and Fe₂O₃ till a mass loss of 25% is reached at 375°C (cal. loss = 25.1%). Corresponding to this step, DTA shows an exotherm at 300°C and the respective DTG peak lies at 302°C. These intermediates remain stable up to 850°C as indicated by the presence of an arrest in TG. The presence of Fe₂O₃ has been confirmed by recording Mössbauer spectrum of the residue obtained by calcining the precursor isothermally at 390°C for 15 min. Mössbauer parameters of the residue were similar to those reported for α-Fe₂O₃ of bulk size [31, 32]. As the heating continues, rubidium acetate undergoes decomposition to yield Rb₂O as indicated by a mass loss of 47.6% at 940°C (cal. loss= 47.3%) and supported by an endotherm that subsequently becomes exotherm to facilitate a solid state reaction between Rb₂O and α-Fe₂O₃ to yield ferrite product. The identity of the ferrite as RbFeO₂ has been revealed by Mössbauer parameters (Table 1) and XRD powder pattern of the final thermolysis product. The formation of ferrite (RbFeO₂) with an average particle size of 65 nm has been confirmed by TEM.

Based on the above results, the following mechanism for the thermal decomposition of rubidium hexa(acetato)ferrate(III) monohydrate is suggested:

\[
\begin{align*}
\text{Rb}_3[\text{Fe(C}_2\text{H}_3\text{COO})_6].\text{H}_2\text{O} & \xrightarrow{103^0\text{C}} \text{Rb}_3[\text{Fe(C}_2\text{H}_3\text{COO})_6] + \text{H}_2\text{O(g)} \\
& \text{dehydration} \\
\text{Rb}_3[\text{Fe(C}_2\text{H}_3\text{COO})_6] & \xrightarrow{375^0\text{C}} \frac{1}{2} \alpha-\text{Fe}_2\text{O}_3 + 3\text{Rb(CH}_3\text{COO)} + \text{gaseous products} \\
& \text{exo-decomp.} \\
3\text{Rb(CH}_3\text{COO)} & \xrightarrow{940^0\text{C}} \frac{3}{2} \text{Rb}_2\text{O} + \text{gaseous products} 
\end{align*}
\]
3.2.2.1.3 Rubidium hexa(propionato)ferrate(III),
\[ \text{Rb}_3[\text{Fe(CH}_3\text{CH}_2\text{COO})_6] \]

Figure 14 exhibits the simultaneous TG-DTG-DTA curves of anhydrous rubidium hexa(propionato)ferrate(III) precursor in flowing air atmosphere at a heating rate of 10\(^{\circ}\)C min\(^{-1}\). The anhydrous precursor undergoes an abrupt oxidative decomposition with a mass loss of 43\% at 380\(^{\circ}\)C suggesting the formation of \(\text{Fe}_2\text{O}_3\) and rubidium carbonate (cal. loss = 43.2\%). Corresponding to this step, DTG shows a peak at 298\(^{\circ}\)C while DTA exhibits an exotherm centered at 290\(^{\circ}\)C. The existence of \(\text{Fe}_2\text{O}_3\) and \(\text{Rb}_2\text{CO}_3\) have been confirmed by recording Mössbauer and IR parameters of the residue obtained by calcining the precursor isothermally at 380\(^{\circ}\)C for 15 min. (Table 1). As heating continues, rubidium carbonate gets decomposed into \(\text{Rb}_2\text{O}\) as supported by an endotherm at 910\(^{\circ}\)C followed by its solid state reaction with \(\alpha\)-\(\text{Fe}_2\text{O}_3\) to give \(\text{RbFeO}_2\) as indicated by a mass loss of 52\% at 950\(^{\circ}\)C (cal. loss = 52.2\%). The exotherm associated with the solid state reaction lies at 980\(^{\circ}\)C. The identity of the end product as \(\text{RbFeO}_2\) has been confirmed from its Mössbauer parameters (Table 1) and XRD powder pattern. TEM analysis reveals the existence of ferrite particles with average size of 75 nm.

Based on the above observations, the following pathway for the aerial thermal decomposition of rubidium hexa(propionato)ferrate(III) precursor is proposed:

\[ \text{380}^{\circ}\text{C} \]
3.2.2.1.4 Rubidium hexa(butyrate)ferrate(III),

\[ \text{Rb}_3[\text{Fe(CH}_3\text{CH}_2\text{COO)}_6] \rightarrow \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{3}{2}\text{Rb}_2\text{CO}_3 + \text{gaseous products} \]

\[ \text{3/2 Rb}_2\text{CO}_3 \rightarrow \frac{3}{2}\text{Rb}_2\text{O} + \frac{3}{2}\text{CO}_2 \text{ by endo-decomp.} \]

\[ \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{1}{2}\text{Rb}_2\text{O} \rightarrow \text{RbFeO}_2 \text{ by endo-decomp.} \]

\[ \text{950}^\circ\text{C} \]

\[ \text{>950}^\circ\text{C} \]
Figure 15 displays the simultaneous TG-DTG-DTA curves of anhydrous rubidium ferributyrate precursor in flowing air atmosphere at a heating rate of 10°C min⁻¹. The thermal decomposition pattern of rubidium hexa(butyrate)ferrate(III) precursor has been found to be almost similar to that observed for its propionate counterpart. The identity of the end product as RbFeO₂ has been revealed by its Mössbauer parameters (Table 1) and XRD powder pattern. TEM study of the final thermolysis product of rubidium ferributyrate precursor shows an average particle size of 80 nm for the ferrite obtained.

The above discussion leads to the following consecutive decomposition steps:

\[
\begin{align*}
285^0\text{C} & \quad \text{Rb}_3[\text{Fe(CH}_3\text{CH}_2\text{CH}_2\text{COO})_6] \quad \xrightarrow{\text{exo-decomp.}} \quad \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + 3\text{Rb(CH}_3\text{CH}_2\text{CH}_2\text{COO)} + \text{gaseous products} \\
875^0\text{C} & \quad 3\text{Rb(CH}_3\text{CH}_2\text{CH}_2\text{COO)} \quad \xrightarrow{\text{exo-decomp.}} \quad \frac{3}{2}\text{Rb}_2\text{CO}_3 + \text{gaseous products} \\
925^0\text{C} & \quad \frac{3}{2}\text{Rb}_2\text{CO}_3 \quad \xrightarrow{\text{endo-decomp.}} \quad \frac{3}{2}\text{Rb}_2\text{O} + \frac{3}{2}\text{CO}_2 \\
>925^0\text{C} & \quad \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{1}{2}\text{Rb}_2\text{O} \quad \xrightarrow{\text{exo-decomp.}} \quad \text{RbFeO}_2
\end{align*}
\]
Fig. 8: Simultaneous TG-DTG-DTA curves of rubidium hexa(formato)ferrate(III) trihydrate precursor.
Fig. 9: Mössbauer spectrum of formate precursor calcined at 380°C for 15 mins.

Fig. 10: XRD powder pattern of the final thermolysis product of formate precursor.
Fig. 11: Mössbauer spectrum of the final thermolysis product of formate precursor.

Fig. 12: TEM Micrograph of the final thermolysis product of formate precursor.
Fig. 13: Simultaneous TG-DTG-DTA curves of rubidium hexa(actetato)ferrate(III) monohydrate.
Fig. 14: Simultaneous TG-DTG-DTA curves of rubidium hexa(propionato)ferrate(III) precursor.
Fig.15: Simultaneous TG-DTG-DTA curves of rubidium hexa(butyrate)ferrate(III) precursor.
Table 1: Mössbauer parameters for the thermolysis products of Rb$_3$[Fe(L)$_6$].xH$_2$O recorded at 300K.

<table>
<thead>
<tr>
<th>L</th>
<th>Temp. of Calcination, °C</th>
<th>$\delta^{w.r.t.}$ mm/s</th>
<th>$\Delta$ mm/s</th>
<th>B (T)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO</td>
<td>380</td>
<td>0.39</td>
<td>0.02</td>
<td>51.4</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>&gt;900</td>
<td>0.37</td>
<td>0.69</td>
<td>---</td>
<td>RbFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$COO</td>
<td>390</td>
<td>0.31</td>
<td>0.04</td>
<td>51.3</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>&gt;950</td>
<td>0.39</td>
<td>0.73</td>
<td>---</td>
<td>RbFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$COO</td>
<td>380</td>
<td>0.31</td>
<td>0.01</td>
<td>51.6</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>&gt;950</td>
<td>0.36</td>
<td>0.69</td>
<td>---</td>
<td>RbFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$COO</td>
<td>300</td>
<td>0.33</td>
<td>0.01</td>
<td>51.5</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
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<tr>
<td></td>
<td>&gt;925</td>
<td>0.39</td>
<td>0.68</td>
<td>---</td>
<td>RbFeO$_2$</td>
</tr>
</tbody>
</table>

$w.r.t.$ pure metallic iron absorber, $\Delta =$ quadrupole shift, B = Internal magnetic field in Tesla (T), S = Sextet, CD = Central doublet
3.2.2.1.5 Characterization of rubidium ferrite obtained from thermolysis of dicarboxylate (oxalate) precursor

IR spectrum of rubidium tris(oxalato)ferrate(III)trihydrate precursor shows a broad band centered around 3280 cm$^{-1}$ due to $\nu$(O-H) of lattice water. A broad band centered at 1590 cm$^{-1}$ is attributed to $\nu_{\text{asym}}$(C=O) while band due to $\nu_{\text{sym}}$(C=O) lies in the range 1385-1460 cm$^{-1}$. A band at 570 cm$^{-1}$ suggests the presence of Fe-O (carboxylate) bonding [29]. Mössbauer spectrum of the precursor exhibits a doublet with isomer shift ($\delta$) and quadrupole splitting ($\Delta$) values of 0.37 and 0.49 mms$^{-1}$ respectively. The coordination number of six for iron is satisfied by three oxalate ligands which bind to iron through oxygen atoms of oxalate groups. The water molecules seem to be responsible for linking together the complex ion, [Fe(ox)$_3$]$^{3+}$.

Figure 16 displays the simultaneous TG-DTG-DTA curves of rubidium ferrioxalate precursor in flowing air atmosphere at a heating rate of 10$^\circ$C min$^{-1}$. TG shows a weight loss of 8.45 % at 125$^\circ$C indicating dehydration of the precursor (cal. loss = 8.4%). The respective DTG and DTA (endo) peaks are centered at 86$^\circ$C and 89$^\circ$C respectively. The anhydrous precursor then undergoes an exothermic decomposition to yield rubidium carbonate and $\alpha$-Fe$_2$O$_3$ till a mass loss of 32.5% is reached at 305°C (cal. loss = 32.7%). Corresponding to this step, strong DTA (exo) and DTG peaks lie at 239°C and 248°C respectively. The existence of Fe$_2$O$_3$ has been confirmed by Mössbauer spectrum of the residue obtained by calcining the precursor isothermally at 305°C for 15 min., which shows a six line pattern (Figure 17) due to magnetic hyperfine interaction with isomer shift and internal magnetic field values of 0.39 mms$^{-1}$ and 54.02 T respectively. These parameters are in agreement with the reported values for $\alpha$-Fe$_2$O$_3$ [31, 32]. The presence of Rb$_2$CO$_3$ has been affirmed by recording the IR spectrum of the residue that showed a characteristic carbonate peak at 1475 cm$^{-1}$. As the heating continues, Rb$_2$CO$_3$ decomposes into Rb$_2$O with the evolution of CO$_2$ as indicated by the presence of an endotherm at 870°C, followed by a solid state reaction between Rb$_2$O and $\alpha$-Fe$_2$O$_3$ as reflected by an exotherm to yield rubidium ferrite, RbFeO$_2$ with a mass loss of 42.40% at 900$^\circ$C (cal. loss = 42.9%). Mössbauer spectrum of the final residue (Figure 16) obtained shows a central doublet with isomer shift and quadrupole splitting values of 0.34 mms$^{-1}$ and 0.83 mms$^{-1}$ respectively. These parameters are in agreement with those reported for analogous cesium ferrite [24-26]. The identity of the ferrite as RbFeO$_2$, has been revealed by Mössbauer parameters (Table 2) and XRD powder pattern.
(Figure 19) of the final thermolysis residue. The average particle size of the ferrite has been found to be 33 nm as displayed by TEM (Figure 20).

On the basis of various physico-chemical studies, the following mechanism for the thermal decomposition of rubidium tris(oxalate)ferrate (III) is proposed:

\[
\begin{align*}
\text{Rb}_3[\text{Fe(C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O} & \xrightarrow{125^\circ\text{C}} \text{Rb}_3[\text{Fe(C}_2\text{O}_4)_3] + 3\text{H}_2\text{O(g)} \\
& \quad \text{dehydration} \\
\text{Rb}_3[\text{Fe(C}_2\text{O}_4)_3] & \xrightarrow{305^\circ\text{C}} \frac{1}{2} \alpha\text{-Fe}_2\text{O}_3 + \frac{3}{2} \text{Rb}_2\text{CO}_3 + \text{gaseous products} \\
\text{Rb}_2\text{CO}_3 & \xrightarrow{900^\circ\text{C}} \frac{3}{2} \text{Rb}_2\text{O} + \text{CO}_2 \\
& \quad \text{exo-decomp.} \\
\frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{1}{2}\text{Rb}_2\text{O} & \xrightarrow{>900^\circ\text{C}} \text{RbFeO}_2
\end{align*}
\]

The unreacted Rb$_2$O was removed by treating the final thermolysis residue with 2N HNO$_3$. 

Fig. 16: Simultaneous TG-DTG curves of rubidium tris(oxalato)ferrate(III) trihydrate precursor.
Fig. 17: Mössbauer spectrum of the residue obtained after calcining the precursor at 305°C for 15 min.

Fig. 18: Mössbauer spectrum of the final thermolysis product
Fig.19: XRD powder pattern of the final thermolysis product of oxalate precursor.

Fig.20: TEM Micrograph of the final thermolysis product of oxalate precursor.
3.2.2.1.6 Characterization of rubidium ferrite obtained from rubidium tricarboxylate (citrate) precursor

IR spectrum of rubidium ferricitrate precursor shows a broad band centered at about 3267 cm\(^{-1}\) due to \(\nu(\text{O-H})\) of lattice water and a distinct shoulder at 2873 cm\(^{-1}\) due to \(\nu(\text{C-H})\) of the citrate group. An intense band at 1610 cm\(^{-1}\) due to \(\nu_{\text{asy}}(\text{C=O})\) and bands in the range 1360-1255 cm\(^{-1}\) due to \(\nu_{\text{sym}}(\text{C=O})\) have been observed for the coordinated citrate groups [28] respectively. Mössbauer spectrum of the rubidium ferricitrate precursor exhibits a single broad absorption band (Figure 21) due to spin lattice relaxation effect [33]. The isomer shift value of 0.33 mms\(^{-1}\) corresponds to that reported for high spin ferric ions in octahedral coordination [30, 34]. The coordination number of six for iron is satisfied by two citrate ligands which bind to iron through oxygen atoms of the citrate groups.

![Mössbauer spectrum of rubidium bis(citrato)ferrate(III) trihydrate precursor.](image)

Fig.21: Mössbauer spectrum of rubidium bis(citrato)ferrate(III) trihydrate precursor.
Figure 22 shows the simultaneous TG-DTG-DTA curves for rubidium bis(citrato)ferrate(III) trihydrate precursor in flowing air atmosphere at a heating rate of 10\(^\circ\)C min\(^{-1}\). The complex undergoes dehydration till a mass loss of 7.20% is reached at 200\(^\circ\)C (cal. loss = 7.23%). The corresponding broad DTA (endotherm) and DTG peaks are centered at about 120\(^\circ\)C. After dehydration, precursor remains stable up to 300\(^\circ\)C as shown by an arrest in TG and subsequently, undergoes exothermic decomposition as supported by a mass loss of 42.4% at 500\(^\circ\)C (cal. loss = 42.7%) that corresponds to the formation of Fe\(_2\)O\(_3\) and rubidium carbonate. The presence of Fe\(_2\)O\(_3\) has been confirmed by recording Mössbauer spectrum of the residue obtained by calcining the precursor isothermally at 500\(^\circ\)C for 15 min. The shape of the spectrum (Figure 23) and Mössbauer parameters (Table 2) resemble to those reported [31, 32] for a cluster of \(\alpha\)-Fe\(_2\)O\(_3\) particles with an average grain size of 15 nm. The particles with diameters less than 15 nm present in the cluster show a central doublet while in case of particles with diameters greater than 15 nm, a hyperfine spectrum arises. The existence of Rb\(_2\)CO\(_3\) has been affirmed by recording the IR spectrum of the residue that displayed a characteristic carbonate peak at 1437 cm\(^{-1}\). At higher temperature, rubidium carbonate decomposes into rubidium oxide with the evolution of CO\(_2\) followed by a solid-state reaction between rubidium oxide and \(\alpha\)-Fe\(_2\)O\(_3\) to yield rubidium ferrite, RbFeO\(_2\) as shown by a mass loss of 51.4% (cal. loss = 51.58%). above 800\(^\circ\)C. Both these thermal changes are reflected by corresponding DTA (endo) and DTG peaks at 750\(^\circ\)C and 810\(^\circ\)C respectively. XRD powder pattern (Figure 24) of the final residue shows the formation of ferrite product. The identity of the ferrite as RbFeO\(_2\) has also been confirmed by recording Mössbauer spectrum (Figure 25) of the final residue. Mössbauer parameters are in close agreement with the reported values for analogous ferrites reported in literature [24-26]. TEM micrograph (Figure 26) reveals that the average particle size of RbFeO\(_2\) obtained is 65 nm.
On the basis of various physico-chemical studies, the following mechanism for the thermal decomposition of rubidium bis citratoferrates (III) is proposed.

\[
\begin{align*}
200^\circ\text{C} & \\
\text{Rb}_3[\text{Fe}(\text{C}_6\text{H}_5\text{O}_7)_2]. 3\text{H}_2\text{O} & \rightarrow \text{Rb}_3[\text{Fe}(\text{C}_6\text{H}_5\text{O}_7)_2] + 3\text{H}_2\text{O}(g) \\
\text{dehydration} & \\
500^\circ\text{C} & \\
\text{Rb}_3[\text{Fe}(\text{C}_6\text{H}_5\text{O}_7)_2] & \rightarrow 1/2\alpha-\text{Fe}_2\text{O}_3 + 3/2\text{Rb}_2\text{CO}_3 + \text{gaseous product} \\
\text{exo-decomp.} & \\
760^\circ\text{C} & \\
3/2\text{Rb}_2\text{CO}_3 & \rightarrow 3/2\text{Rb}_2\text{O} + 3/2\text{CO}_2 \\
\text{endo-decomp.} & \\
800^\circ\text{C} & \\
1/2\alpha-\text{Fe}_2\text{O}_3 + 1/2\text{Rb}_2\text{O} & \rightarrow \text{RbFeO}_2
\end{align*}
\]
Table 2: Mössbauer parameters for the thermolysis products of Rb$_3$[Fe(ox)$_3$].xH$_2$O and Rb$_3$[Fe(cit)$_2$].xH$_2$O recorded at 300K.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temp. of Calcination, °C</th>
<th>$\delta^a$ mm/s</th>
<th>$\Delta$ mm/s</th>
<th>B (T)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_3$[Fe(C$_2$O$_4$)$_3$].3H$_2$O</td>
<td>305</td>
<td>0.39</td>
<td>0.01</td>
<td>54.02</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>&gt;900</td>
<td>0.34</td>
<td>0.83</td>
<td>----</td>
<td>RbFeO$_2$</td>
</tr>
<tr>
<td>Rb$_3$[Fe(C$_6$H$_5$O$_7$)$_2$].3H$_2$O</td>
<td>500</td>
<td>0.34</td>
<td>0.03</td>
<td>51.09</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.31</td>
<td>0.43</td>
<td>----</td>
<td>RbFeO$_2$</td>
</tr>
</tbody>
</table>

$^a$w.r.t. pure metallic iron absorber, $\Delta$ = quadrupole shift, B = Internal magnetic field in Tesla (T),

S = Sextet, CD = Central doublet
Fig.22: Simultaneous TG-DTG-DTA curves for rubidium bis(citrato)ferrate(III) trihydrate precursor.
Fig. 23: Mössbauer spectrum of precursor calcined at 500 °C for 15 mins.

Fig. 24: XRD powder pattern for the final thermolysis product of citrate precursor.
Fig. 25: Mössbauer spectrum for the final thermolysis product of citrate precursor.

Fig. 26: Transmission Electron Micrograph of the final thermolysis product of citrate precursor.
3.2.3 Characterization of cesium ferrite obtained from cesium ferrimonocarboxylates:

IR spectrum of cesium hexa(formato)ferrate(III) monohydrate precursor shows a broad band centered at about 3273 cm$^{-1}$ due to $v$(O-H) of lattice water and a distinct shoulder at 2881 cm$^{-1}$ due to $v$(C-H) of the formate group. Intense bands in the ranges 1625-1660 cm$^{-1}$ and 1370-1415 cm$^{-1}$ are attributed to $v_{\text{asy}}$(C=O) and $v_{\text{sym}}$(C=O) of the coordinated formate groups [28]. A small but distinct band at 587 cm$^{-1}$ due to $v$(Fe-O) suggests the presence of Fe-O (carboxylate) bonding [29]. The other ferrimonocarboxylates (acetate, propionate and butyrate) display almost similar IR spectra except the presence of $v$(O-H) of the lattice water as these are anhydrous.

Mössbauer spectra of the cesium ferricarboxylate precursors exhibit a doublet (Figure 27) with isomer shift ($\delta$) and quadrupole splitting ($\Delta$) values in the ranges 0.33-0.37 mms$^{-1}$ and 0.46-0.60 mms$^{-1}$ respectively. These parameters correspond to those reported for high spin Fe$^{3+}$ ions in octahedral coordination [30]. The asymmetry of the intensity of quadrupole lines may be attributed to the prefential orientation, a phenomenon common in polycrystalline iron materials.

Fig. 27: Mössbauer spectrum of cesium hexa(formato)ferrate(III) monohydrate precursor.
3.2.3.1 Thermal decomposition studies

A compoundwise discussion on the thermal decomposition of various cesium hexa(carboxylato)ferrate(III) precursors follows:

3.2.3.1.1 Cesium hexa(formato)ferrate(III) monohydrate,

\[ \text{Cs}_3[\text{Fe(HCOO)}_6].\text{H}_2\text{O} \]

Figure 22 shows the simultaneous TG-DTG-DTA curves of cesium hexa(formato)ferrate(III) monohydrate in flowing air atmosphere at a heating rate of 10$^\circ$C min$^{-1}$. The precursor undergoes dehydration till a mass loss of 2.3% is reached at 128$^\circ$C (cal. loss = 2.5%). The corresponding broad DTA (endotherm) and DTG peak maxima are centered at about 108$^0$C and 110$^0$C respectively. The anhydrous precursor undergoes exothermic decomposition to yield cesium carbonate and Fe$_2$O$_3$ until a mass loss of 23.6% is reached at 360$^0$C (cal. loss = 23.4%). Corresponding to this step, DTA shows an exotherm at 282$^0$C while DTG also displays a respective distinct signal at 268$^0$C. The presence of Fe$_2$O$_3$ has been confirmed by recording the Mössbauer spectrum (Figure 29) of the residue obtained by calcining the precursor isothermally at 400$^0$C for 15 min. The spectrum shows a six line pattern (sextet) due to magnetic hyperfine interactions and Mössbauer parameters of the residue (Table 3) resemble to those reported for $\alpha$-Fe$_2$O$_3$ of bulk size [31, 32]. The existence of cesium carbonate has been affirmed by recording IR spectrum of the residue that displayed a characteristic carbonate peak at 1435 cm$^{-1}$ [28, 29]. As the heating continues, Cs$_2$CO$_3$ decomposes into Cs$_2$O as indicated by a mass loss of 32.2% at 700$^0$C (cal. loss= 32.3%) followed by a solid state reaction between Cs$_2$O and $\alpha$-Fe$_2$O$_3$ to yield cesium ferrite i.e. CsFeO$_2$. Both these thermal changes are reflected by the corresponding endotherm and exotherm with peak maxima at 680$^0$C and 764$^0$C respectively. DTG also shows respective signal for the endo-decomposition of cesium carbonate into cesium oxide at 685$^0$C. The identity of the ferrite has been confirmed by recording Mössbauer spectrum (Figure 30) of the final residue, which shows a doublet with hyperfine parameters $\delta$=0.34 mms$^{-1}$ and $\Delta$=0.72 mms$^{-1}$. These parameters (Table 3) are in agreement to the ones reported for CsFeO$_2$ [24-26]. XRD powder pattern (Figure 31) of the final thermolysis residue also reveals the existence of CsFeO$_2$ with CsAlO$_2$ type geometry [27]. TEM analysis (Figure 32) of the end product exhibits the formation of ferrite with average particle size of 55 nm.
Based on the above discussion, the following pathway for the thermal decomposition of cesium hexa(formato)ferrate(III) trihydrate precursor is proposed:

\[
\begin{align*}
\text{Cs}_3[\text{Fe(HCOO)}_6].\text{H}_2\text{O} & \quad \xrightarrow{128^0\text{C}} \quad \text{Cs}_3[\text{Fe(HCOO)}_6] + \text{H}_2\text{O}(g) \\
\quad \text{dehydration} & \\
\text{Cs}_3[\text{Fe(HCOO)}_6] & \quad \xrightarrow{360^0\text{C}} \quad \frac{3}{2}\text{Cs}_2\text{CO}_3 + \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \text{gaseous} \\
\quad \text{exo-decomp.} & \\
\frac{3}{2}\text{Cs}_2\text{CO}_3 & \quad \xrightarrow{700^0\text{C}} \quad \frac{3}{2}\text{Cs}_2\text{O} + \frac{3}{2}\text{CO}_2 \\
\quad \text{endo-decomp.} & \\
\frac{1}{2}\text{Cs}_2\text{O} + \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 & \quad \xrightarrow{>800^0\text{C}} \quad \text{CsFeO}_2
\end{align*}
\]

The final thermolysis residue was treated with conc. HNO\textsubscript{3} for removing the unreacted Cs\textsubscript{2}O and obtaining pure CsFeO\textsubscript{2} ferrite.
3.2.3.1.2 Cesium hexa(acetato)ferrate(III), Cs₃[Fe(CH₃COO)₆].

Figure 33 presents the simultaneous TG-DTG-DTA curves of anhydrous cesium hexa(acetato)ferrate(III) at a heating rate of 10⁰C min⁻¹. After remaining stable up to 140⁰C, the anhydrous precursor undergoes an exothermic decomposition to yield cesium carbonate and Fe₂O₃ till a mass loss of 29.4% is reached at 320⁰C (cal. loss = 29.6%). Corresponding to this step, DTA shows an exotherm at 245⁰C while the respective DTG peak lies at 252⁰C. The existence of cesium carbonate and α-Fe₂O₃ have been affirmed by recording IR spectrum that showed a characteristic carbonate peak at 1430 cm⁻¹ and Mössbauer parameters (Table 3) of the residue obtained by isothermal calcination of the precursor at 320⁰C for 15 min. After remaining stable up to 650⁰C, cesium carbonate undergoes endo-decomposition to yield Cs₂O as indicated by a mass loss of 37.4% at 740⁰C (cal. loss = 37.8%) and supported by an endotherm at 700⁰C. This step is also accompanied by a DTG signal with peak maxima at 705⁰C. Subsequent heating leads to a solid state reaction between α-Fe₂O₃ and Cs₂O (supported by an exotherm at 820⁰C) to give the ferrite product. The identity of the ferrite as CsFeO₂ has been revealed by Mössbauer parameters (Table 3) and XRD powder pattern of the final thermolysis product. The formation of ferrite (CsFeO₂) with an average particle size of 60 nm has been confirmed by TEM.

Based on the above results, the following mechanism for the thermal decomposition of cesium hexa(acetato)ferrate(III) is suggested:

\[
\begin{align*}
320^\circ C & \quad \text{Cs}_3[\text{Fe(CH}_3\text{COO)}_6] \quad \text{exo-decomp.} \\
& \quad \quad \longrightarrow \alpha-\text{Fe}_2\text{O}_3 + 3/2\text{Cs}_2\text{CO}_3 + \text{gaseous products} \\
740^\circ C & \quad 3/2\text{Cs}_2\text{CO}_3 \quad \text{endo-decomp.} \\
& \quad \quad \longrightarrow 3/2\text{Cs}_2\text{O} + 3/2\text{CO}_2 \\
840^\circ C & \quad 1/2 \alpha-\text{Fe}_2\text{O}_3 + 1/2 \text{Cs}_2\text{O} \quad \longrightarrow \text{CsFeO}_2
\end{align*}
\]
Fig. 26: Simultaneous TG-DTG-DTA curves of cesium hexa(formato)ferrate(III) monohydrate precursor.
Fig. 29: Mössbauer spectrum of the residue obtained after calcining the precursor at 400°C for 15 min.

Fig. 24: Mössbauer spectrum of the final thermolysis product of formate precursor.
Fig. 31: XRD powder pattern of the final thermolysis product of formate precursor.

Fig. 32: TEM Micrograph of the final thermolysis product of formate precursor.
Fig.33: Simultaneous TG-DTG-DTA curves of cesium hexaactetato ferrate(III) precursor
3.2.3.1.3 Cesium hexa(propionato)ferrate(III),
Cs$_3$[Fe(CH$_3$CH$_2$COO)$_6$]. 4H$_2$O

Figure 34 exhibits the simultaneous TG-DTG-DTA curves of anhydrous cesium hexa(propionato)ferrate(III) at a heating rate of 10$^0$C min$^{-1}$. Anhydrous cesium ferripropionate precursor undergoes exothermic decomposition to yield cesium propionate and Fe$_2$O$_3$ till a mass loss of 21.6% is reached at 230$^0$C (cal. loss = 21.8%). Corresponding to this step, DTA shows an exotherm at 180$^0$C and the respective DTG peak lies at 167$^0$C. Cesium propionate formed during the decomposition process undergoes immediate breakdown into Cs$_2$CO$_3$ with a mass loss of 36.2% at 325$^0$C (cal. loss = 36.3%). The existence of Cs$_2$CO$_3$ and $\alpha$-Fe$_2$O$_3$ have been confirmed by recording IR and Mössbauer parameters of the residue (Table 3) obtained by isothermal calcination of the precursor at 325$^0$C for 15 min. Finally, at higher temperature (750$^0$C), Cs$_2$CO$_3$ undergoes decomposition into Cs$_2$O, followed by its solid state reaction with $\alpha$-Fe$_2$O$_3$ to yield ferrite product at 840$^0$C. These steps are accompanied by a characteristic endotherm at 725$^0$C and an exotherm at 800$^0$C respectively. DTG also shows a corresponding signal at 732$^0$C. The identity of the ferrite as CsFeO$_2$ has been revealed by Mössbauer parameters (Table 3) and XRD powder pattern of the final thermolysis product. An average particle size of 75 nm has been calculated from TEM micrograph for the ferrite obtained.

Based on the above observations, the following pathway for the aerial thermal decomposition of cesium hexa(propionato)ferrate(III) precursor is proposed:

\[
\begin{align*}
230^0C \\
\text{Cs}_3[\text{Fe(\text{CH}_3\text{CH}_2\text{COO})}_6] &\xrightarrow{\text{exo-decomp}} 1/2 \alpha-\text{Fe}_2\text{O}_3 + 3 \text{Cs(\text{CH}_3\text{CH}_2\text{COO})} + \text{gaseous products} \\
325^0C \\
3 \text{Cs(\text{CH}_3\text{CH}_2\text{COO})} &\xrightarrow{} 3/2 \text{Cs}_2\text{CO}_3 + \text{gaseous product}
\end{align*}
\]
3.2.3.1.4 Cesium hexa(butyrate)ferrate(III),
Cs₅[Fe(CH₃CH₂CH₂COO)₆].

The thermal decomposition pattern of cesium hexa(butyrate)ferrate(III) precursor has been found to be almost similar to that observed for its propionate counterpart. The identity of the end product as CsFeO₂ has been revealed by its Mössbauer parameters (Table 3) and XRD powder pattern. TEM study of the final thermolysis product shows the presence of an average particle size of 85 nm.

Detailed investigations on preparation and characterization of cesium tris(oxalate) ferrate (III) and cesium bis (citrate) precursors have already been reported by our group [24, 25], therefore, these studies are not being included in this section.
Fig. 34: Simultaneous TG-DTG-DTA curves of cesium hexa(propionato)ferrate(III) precursor.
Table 3: Mössbauer parameters for the thermolysis products of Cs$_3$[Fe(L)$_6$].xH$_2$O recorded at 300K.

<table>
<thead>
<tr>
<th>L</th>
<th>Temp. of Calcination °C</th>
<th>δ* mm/s</th>
<th>Δ mm/s</th>
<th>B (T)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO</td>
<td>360</td>
<td>0.32</td>
<td>0.003</td>
<td>50.3</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>0.34</td>
<td>0.72</td>
<td>-----</td>
<td>CsFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$COO</td>
<td>320</td>
<td>0.31</td>
<td>-0.01</td>
<td>50.9</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>0.39</td>
<td>0.81</td>
<td>---</td>
<td>CsFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$COO</td>
<td>325</td>
<td>0.30</td>
<td>0.001</td>
<td>51.6</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>0.36</td>
<td>0.76</td>
<td>---</td>
<td>CsFeO$_2$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$COO</td>
<td>325</td>
<td>0.33</td>
<td>0.02</td>
<td>51.5</td>
<td>α-Fe$_2$O$_3$</td>
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<tr>
<td></td>
<td>850</td>
<td>0.39</td>
<td>0.83</td>
<td>---</td>
<td>CsFeO$_2$</td>
</tr>
</tbody>
</table>

*# w.r.t. pure metallic iron absorber, Δ = quadrupole shift, B = Internal magnetic field in Tesla (T), S = Sextet, CD = Central doublet
3.3 Conclusions:
Single phase MFeO$_2$ (M= Rb, Cs) powders have been successfully prepared by precursor as well as combustion methods.

A). From the various physico-chemical studies adopted for the thermolysis of various metal ferricarboxylate/oxalate/citrate precursors, the following conclusions can be drawn:
The thermal decomposition of the alkali metal precursors occur in the following major consecutive steps:

i) Dehydration of the precursors (except for the anhydrous precursors).

ii) Endo-decomposition of anhydrous metal precursor into Fe$_2$O$_3$ and metal oxides.

iii) Solid state reaction between metal oxide and Fe$_2$O$_3$ to yield final ferrite product.

B). Metal ferrites have also been prepared by the solution combustion method which involves a direct mixing of the cations on atomic scale. Oxalyl dihydrazide (ODH) and urea used in this method act as fuel for the combustion synthesis of ferrites. An enormous amount of heat and gases (CO$_2$, N$_2$, H$_2$O vapour) liberated during the exothermic redox chemical reaction, not only reduces the external temperature required for the preparation of ferrites but also dissipates the heat, thus, inhibiting the sintering of fine ferrite particles. Ferrite prepared by combustion method have smaller particle size than those obtained from precursor method. Additionally, the yield for the ferrite product is higher in case of solution combustion method as compared to precursor method.

In comparison to other conventional ceramic method viz. (i) Ferrites are formed at lower temperature and in shorter time, (ii) The generation of high reaction temperature which can volatilize low boiling point impurities and, therefore, result in high purity products, (iii) The simple exothermic nature of the combustion reaction avoids the need for expensive processing facilities and equipment, (iv) Ferrite particles of small size and greater surface area are obtained. (v) No milling of starting materials is required (necessary in ceramic method) that can introduce lattice defects in the ferrite obtained which, in turn, affect its permanent magnetic properties.
References