CHAPTER – IV

Characterization of mixed alkali metal ferrites, \( \text{M}_{0.5-\text{X}/2}\text{Zn}_{\text{X}}\text{Mn}_{0.05}\text{Fe}_{2.45-\text{X}/2}\text{O}_4 \) (M=Rb, Cs)

4.1 Introduction:

Ferrites are regarded as better magnetic materials than pure metals because of their low cost, high resistivity and ease of preparation and it has been found that small addition of dopants can improve their magnetic properties. Immense technological significance of ferrites lies in the fact that these are the important magnetic materials of modern electronic industry. Magnetic materials belonging to mixed alkali metal ferrites find extensive use in microwave components due to their attractive electrical and magnetic properties [1-11]. The properties of the ferrite materials, which decide the application areas, are generally governed by the chemical compositions and the procedures followed for their preparation. Therefore, the molecular engineering of ferrite composition and employment of appropriate process parameters play a significant role in tailoring the material properties for a specific need. The properties of the ferrites can be modified and upgraded by substituting the optimum amount of various metal ions in the basic compositional formulae. In this way, ferrites provide a wide range of properties and are useful for a variety of applications. It is, therefore, desirable to investigate and understand the dependence of composition on magnetic/electric behaviour of these ferrites. Ferrite nanoparticles show unusual magnetic properties such as single domain behaviour and superparamagnetism which are not observed in bulk material [12,13]. Therefore, chemical aspect has become the most important factor in the design and preparation of ferrite materials. Solution combustion method has been found to be the most suitable technique for the synthesis of a particular mixed ferrite composition. The properties of the final product (particle size, surface area, and porosity) depend on the way the combustion is conducted. The departure of gases favours the desegregation of the products (increasing the porosity) and heat dissipation (inhibiting the sintering of the products). The exothermicity of the combustion is controlled by the nature of the fuel used and the ratio of oxidizer to fuel.

Microstructural studies of materials are essential, because they correlate the physical properties of materials with their microstructure. These properties are also considered important
for the selection of material for device application. Since a detailed investigation has been made on synthesis, characterization and magnetic/microstructural studies of mixed M-Zn (M=Li, Na and K) ferrites [14], similar work on mixed Rb-Zn and Cs-Zn counterparts have been undertaken to make a comparative study.

4.2 Results and discussion:
A compoundwise discussion on the following series prepared by solution combustion method follows:

4.2.1 Mixed rubidium ferrites of composition $\text{Rb}_{0.5-x/2}\text{Zn}_{x}\text{Mn}_{0.05}\text{Fe}_{2.45-x/2}\text{O}_4$

4.2.1.1 XRD studies

Figure 1 shows the X-ray diffraction patterns for different compositions of mixed rubidium ferrites ($\text{Rb}_{0.5-x/2}\text{Zn}_x\text{Mn}_{0.05}\text{Fe}_{2.45-x/2}\text{O}_4$) where $x$ varies from 0 to 0.5. The diffraction peaks (220), (311), (400), (422), (511) and (440) reveal the existence of only single phase cubic spinel ferrite and are comparable to those reported for respective lithium ferrites [15]. IR spectra of all the samples display two main bands in the region $\nu_1$ (630-550 cm$^{-1}$) and $\nu_2$ (525-390 cm$^{-1}$) attributed to stretching vibrations of M-O bond in tetrahedral and octahedral sites [16-18] respectively.

4.2.1.1.1 Lattice constant

Table 1 shows the variation of lattice constant as a function of ‘x’. The value of lattice constant increases with increasing Zn content (x) in the composition. The lattice constant ‘a’ can be calculated theoretically by the following relation[19]:

$$a = (8/3 \sqrt{3}) [(r_A + r_O) + \sqrt{3}(r_B + r_A)]$$

where $r_O$ is the radius of oxygen ion, $r_A$ and $r_B$ are the ionic radii of tetrahedral (A) and octahedral (B) site respectively. This clearly indicates that there exists a correlation between the ionic radii and the lattice constant. In order to estimate $r_A$ and $r_B$ for more than one ion present at a site, it is necessary to know the cationic distribution of the composition. According to the thumb rule if the radius of the substituted ion is smaller than that of the displaced ion, the lattice shrinks and the lattice constant gets reduced. Similarly when the substituted ion of larger ionic radius replaces the metallic ion of smaller ionic radius from the regular lattice, the lattice
constant is expected to increase. **Figure 2** shows the variation of lattice constant with Zn content i.e. a regular increase with increase in the ‘x’ value. This is attributed to the substitution of larger Zn$^{2+}$ cation (0.083nm) for smaller Fe$^{3+}$ cation (0.067 nm). Rubidium ferrites, like other alkali metal ferrites [19] have inverse spinel structure in which all the Rb$^+$ ions occupy octahedral position along with half of the Fe$^{3+}$ ions and remaining Fe$^{3+}$ ions occupy tetrahedral site. The addition of Zn$^{2+}$ ions which have strong affinity for tetrahedral site, only Fe$^{3+}$ ions present at tetrahedral site get replaced, resulting in an increase in lattice parameter. The inverse spinel structure of the ferrite is also supported by the cationic distribution obtained from Mössbauer spectral data.

**4.2.1.1.2 X-ray density**

The theoretical or X-ray density (d$_{\text{XRD}}$) of the prepared rubidium series has been calculated by using the relationship:

$$d_{\text{XRD}} = \frac{8M}{Na^3}$$

Where $M$ is Molecular weight of the ferrite, $N$ is Avogadro’s number and ‘a’ is lattice constant obtained from the different XRD patterns. **Figure 3** exhibits the variation of theoretical and experimental densities as a function of Zn content and shows a regular decrease with increasing ‘x’ value. This may be attributed to a decrease in molecular weight of the ferrite compositions.

**4.2.1.1.3 Experimental density**

The experimental/bulk density (d$_{\text{exp}}$) has been measured for each prepared composition by Archimedes principle. The magnitude of observed and calculated densities have been found to be comparable. Both parameters show a downward trend with increasing magnitude of ‘x’. However, the X-ray density for any given composition is higher than that of the experimental density and this difference is primarily due to the porosity of the material.
4.2.1.4 Porosity
The percentage porosity for all the compositions was calculated by using the equation:

\[1 - \frac{d_{\text{exp.}}}{d_{\text{XRD}}} \times 100\]

The calculated value of the porosity (table 1) have been found to be quite low which is a characteristic requirement of a good quality ferrite material.

4.2.1.5 Particle size
The particle size has been calculated from the XRD data by using Scherrer formula[21]

\[D = \frac{\lambda}{\beta \cos \theta}\]

where \(\lambda\) is the wavelength of x-ray used and ‘\(\beta\)’ is the full width of diffraction line at half maximum and \(\theta\) is the Bragg’s angle. The particle size calculated from XRD powder data and TEM studies reveal the formation of nanosized ferrite particles (Figures 4 & 5).

The percentage of elements present in different compositions were estimated from EDXRF graphs (Figures 6 & 7), and the values obtained agreed with the calculated ones (within ±5% error).
Fig. 1: X-ray powder diffraction patterns for different compositions.
Fig. 2: Variation of Lattice constant ‘a’ with Zn content (x)

Fig. 3: Variation of theoretical (d_{XRD}) and experimental density (d_{EXP.}) with Zn content (x)
Fig. 4: TEM micrograph of $\text{Rb}_{0.5-x/2} \text{Zn}_x \text{Mn}_{0.05} \text{Fe}_{2.45-x/2} \text{O}_4$ with $x=0.3$

Fig. 5: TEM micrograph of $\text{Rb}_{0.5-x/2} \text{Zn}_x \text{Mn}_{0.05} \text{Fe}_{2.45-x/2} \text{O}_4$ with $x=0.5$
Fig. 6: EDXRF graph for the composition $x = 0.3$

Fig. 7: EDXRF graph for the composition $x = 0.5$
Table 1: Variation of various XRD parameters with composition ‘x’ for Rb$_{0.5-x/2}$Zn$_x$Mn$_{0.05}$Fe$_{2.45-x/2}$O$_4$.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Molecular weight (d$_{XRD}$) g/cm$^3$</th>
<th>Density (d$_{Exp}$) g/cm$^3$</th>
<th>Porosity (%)</th>
<th>Lattice parameter ‘a’</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>246.70</td>
<td>5.613</td>
<td>5.331</td>
<td>5.03</td>
</tr>
<tr>
<td>0.1</td>
<td>246.16</td>
<td>5.581</td>
<td>5.329</td>
<td>4.50</td>
</tr>
<tr>
<td>0.2</td>
<td>245.63</td>
<td>5.545</td>
<td>5.285</td>
<td>4.62</td>
</tr>
<tr>
<td>0.3</td>
<td>245.09</td>
<td>5.499</td>
<td>5.249</td>
<td>4.54</td>
</tr>
<tr>
<td>0.4</td>
<td>244.56</td>
<td>5.462</td>
<td>5.172</td>
<td>5.30</td>
</tr>
<tr>
<td>0.5</td>
<td>244.02</td>
<td>5.415</td>
<td>5.132</td>
<td>5.37</td>
</tr>
</tbody>
</table>
4.2.1.2 Magnetic studies

4.2.1.2.1 Saturation magnetization

The magnetic studies of the samples were performed on Vibrating Sample Magnetometer (VSM). Being ferrimagnetic materials, ferrites have non-linear initial magnetization curves as the changing magnetization with applied field is due to a change in the magnetic domain structure. Similar to ferroelectrics, these materials also show hysteresis in their magnetization-magnetic field curve below the Curie point, $T_C$. The magnetization does not return to zero when the applied magnetic field approaches to zero once a large magnetic field is applied. The hysteresis loops traced at room temperature for all the compositions of ‘x’ are displayed in Figure 8. Figure 9 shows the variation of saturation magnetization as a function of Zn content. It has been observed that saturation magnetization increases initially up to a certain level of substitution and then follows the reverse trend. The observed variation can be explained on the basis of exchange interactions [22]. The saturation magnetization can be calculated as

$$ M_S = M_B - M_A $$

Where $M_B$ is the net magnetic moment of ions on B site and $M_A$ is the net magnetic moment of ions on A site. It is well known that if a diamagnetic substituent ion occupies the A site in the spinel, it initially increases the magnetization up to a certain level of substitution and then follows a downward trend. Since non-magnetic Zn$^{2+}$ ion has a strong affinity for A site, its substitution reduces the magnetization of A sub lattice ($M_A$) and thereby increases the net $M_S$ value. It reaches a maximum at $x=0.1$, and afterwards reverses its course (Table 2). The fall in magnetization on addition of Zn beyond this limit can be attributed to the fact that A-sublattice is so much diluted that the A–B interaction becomes weaker than the B–B interaction. This disturbs the parallel alignment of spin magnetic moments on B-site, thus paving way to the Y-K model with canted spins [23]. This model consists of a triangular arrangement of the spins on the sublattices. Many of the magnetic properties of the ferrimagnetic spinel compounds are well understood on the basis of Neel’s collinear model but for the mixed ferrites, the spontaneous magnetization is lower than expected from this model and is usually explained by Yafet-Kittel triangular arrangement.
Fig. 8: Hysteresis loops for different compositions of $\text{Rb}_{0.5-X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$.

Fig. 9: Variation of saturation magnetization with increasing value of ‘x’
4.2.1.2 Curie Temperature

The variation of Curie temperature ($T_C$) with the substitution of non-magnetic Zn$^{2+}$ ion content (x) in the basic compositional formula has been studied. Figure 10 shows a regular decrease in Curie temperature with increase in Zn$^{2+}$ ion content (x) which can be explained on the basis of exchange interactions [22]. An increase in the concentration of diamagnetic Zn$^{2+}$ ions weakens the inter-site exchange interaction due to reduction in the number of magnetic linkages and consequently a fall in Curie temperature. Similar trend has already been reported for different systems [14, 24-26]. The Curie temperatures for various compositions are listed in Table 2.

![Figure 10: Variation of Curie temperature with increasing value of ‘x’](image-url)
Table 2: Variation of Saturation magnetization, Average particle size, Curie’s temperature and dc- resistivity with composition ‘x’ for Rb_{0.5-X/2} Zn_{X} Mn_{0.05} Fe_{2.45-X/2} O_{4} 

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Saturation Magnetization Ms(emu/g)</th>
<th>Average particle size (XRD) (nm)</th>
<th>Curie’s temperature (°C)</th>
<th>Resistivity (Ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.195</td>
<td>8.1</td>
<td>437</td>
<td>4.26*10^5</td>
</tr>
<tr>
<td>0.1</td>
<td>35.463</td>
<td>13.3</td>
<td>370</td>
<td>5.6*10^5</td>
</tr>
<tr>
<td>0.2</td>
<td>32.832</td>
<td>12.8</td>
<td>298</td>
<td>7.2*10^5</td>
</tr>
<tr>
<td>0.3</td>
<td>28.646</td>
<td>11.6</td>
<td>245</td>
<td>2.1*10^6</td>
</tr>
<tr>
<td>0.4</td>
<td>25.497</td>
<td>11.5</td>
<td>180</td>
<td>3.2*10^6</td>
</tr>
<tr>
<td>0.5</td>
<td>21.843</td>
<td>11.2</td>
<td>105</td>
<td>7.70 *10^6</td>
</tr>
</tbody>
</table>
4.2.1.3 Electrical properties

4.2.1.3.1 dc-Electrical Resistivity

The dc-electrical resistivity of the ferrite nanoparticles have been studied at room temperature. A regular increase in resistivity with Zn content (Figure 11) can be explained on the basis of Verwey mechanism of electron hopping [27]. According to this model, ferrites form closed packed oxygen lattice with metal ions located at tetrahedral (A-site) and octahedral (B-site) sites and since A-B distance is greater than the B-B distance, the dominant mode of conduction due to hopping of Fe$^{2+}$ and Fe$^{3+}$ occurs at B site. It has been concluded that electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions results in local displacement of charges which is responsible for the polarization in ferrites and its magnitude depends upon concentration of Fe$^{2+}$ and Fe$^{3+}$ ion pairs present on the B site. The evaporation of metal ion during sintering at higher temperature is mainly responsible for the excess concentration of Fe$^{2+}$ ions in substituted alkali metal ferrites [28]. When Rb$^+$ ion is removed from a region in the crystal lattice and assuming that unit cell retains its full complement of 32 O$^{2-}$ ions, the positive charge of the departed Rb$^+$ must be compensated. This is accomplished by diffusion of Fe$^{3+}$ ion from the surface as the O$^{2-}$ ion on the surface is removed. However, charge neutrality is maintained by the concurrent reduction of that ion from Fe$^{3+}$ to Fe$^{2+}$. Therefore, a partial substitution of the Fe$^{3+}$ ion on the octahedral site by other ions is expected to result in a change in electric properties of the ferrite materials. The higher value of dc-resistivity obtained may be contributed to nanosized ferrite particles obtained by solution combustion method. Samples with smaller particles consist of more number of grain boundaries which act as barriers to the flow of electrons. Another advantage of small size is that it helps in reducing Fe$^{2+}$ ion concentration as oxygen moves faster in small grains keeping iron in Fe$^{3+}$ state.

The temperature dependence of dc-resistivity was also studied in the temperature range 308-398 K as displayed in Figure 12, shows an almost linear decrease in resistivity with temperature suggesting semiconductor behaviour of the ferrite materials in accordance with the Arrhenious relation:

$$\rho = \rho_a \exp\left(\frac{E_\rho}{kT}\right)$$

Where $\rho =$ Resistivity, $\rho_a =$ Resistivity extrapolated to $T = \alpha$
$E_\rho =$ Activation energy, $k =$ Boltzmann’s constant, $T =$ Absolute temperature

113
4.2.1.3.2 Dielectric and Tangent loss studies

Dielectric and tangent loss studies were carried out using LCR meter. Figures 13 & 14 show variation of dielectric constant of ferrite samples with frequency and it is observed that the value of dielectric constant decreases regularly with increase in the frequency. It is clear from the Figures 11 & 13 that the variation of dc-resistivity and dielectric constant as a function of Zn content are having trend opposite to each other. A similar trend has been reported by several workers [29, 30] who have established a strong relationship between conduction mechanism and dielectric behaviour of ferrites. The decrease in dielectric value is rapid at lower frequency and slower at higher frequency which is a common feature of ferrimagnetic behaviour [31,32]. A more dielectric dispersion has been observed at lower frequency range and it remains almost independent of applied external field at high frequency domain. The dielectric dispersion at low frequency is due to Maxwell-Wagner type interfacial polarization [33,34], well in agreement with Koop’s phenomenological theory [35]. Ferrite samples with heterogenous structure can be imagined as systems consisting of high conductive grains separated by highly resistive thin grain boundaries. It causes localized charge accumulation under applied electric field which results in interfacial polarization. At higher frequencies, the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions cannot follow the alternating field, thus, causing a decrease in the contribution of interfacial polarization to dielectric constant and results in a decrease in the dielectric constant at higher frequencies. Figures 15 & 16 show an initial increase in the value of Tangent loss ($\delta$) to attain a maxima followed by a regular decrease with frequency. Such peak behaviour occurs when jump frequency of electron exchange between Fe$^{2+}$ and Fe$^{3+}$ becomes equal to the applied field [36,37].
Fig. 11: Variation of dc-resistivity with Zn content

Fig. 12: Temperature dependence of dc-electrical resistivity of ferrite samples.
Fig. 13: Variation of dielectric constant with frequency (composition x=0.1)

Fig. 14: Variation of dielectric constant with frequency (composition x=0.5)
Fig. 15: Variation of tangent loss ($\delta$) with frequency ($x=0.1$)

Fig. 16: Variation of tangent loss ($\delta$) with frequency ($x=0.5$)
4.2.1.4 Mössbauer studies

Figures 17-22 display Mössbauer spectra for various compositions of ‘x’ for Rb$_{0.5-x/2}$Zn$_x$Mn$_{0.05}$Fe$_{2.45-x/2}$O$_4$. Mössbauer parameters recorded at room temperature are listed in Table-3. Room temperature spectrum for the composition with $x = 0$ (Figure 17) exhibits two well resolved Zeeman sextets arising due to the Fe$^{3+}$ ions present at both tetrahedral and octahedral sites (A and B sites) indicated by red and blue lines respectively. The cationic distribution of Fe$^{3+}$ ion (Table 3) in tetrahedral and octahedral sites is nearly same which may be attributed to inverse spinel structure of the ferrite obtained. With the addition of diamagnetic Zn$^{2+}$ content, Mössbauer spectra show the presence of central paramagnetic doublet superimposed on the sextets and its intensity goes on increasing with further increase in Zn$^{2+}$ concentration as shown in Figures 18-22, also reflected in Figure 23. The central doublet may be attributed to the Fe$^{3+}$ ions which are magnetically isolated and did not participate in long-range magnetic ordering due to the presence of large number of nonmagnetic nearest neighbors (Zn$^{2+}$ ions). Thus, there is a transition from ferrimagnetism to superparamagnetism with increasing diamagnetic Zn content. For diamagnetically substituted ferrites, the existence of a central doublet superimposed on well-resolved magnetic sextets has been reported for a number of systems [14, 38-40]. In the present system, the central doublet arises due to the magnetically isolated Fe$^{3+}$ ions located at the tetrahedral site and not because of any secondary phase. As expected, the isomer shift for the octahedral site is slightly greater than that of tetrahedral site. The isomer shift value at the two sites is different because of the fact that Fe$^{3+}$- O$^{2-}$ distance is implying difference in covalency of Fe-O bond. The variation in magnetic hyperfine field at A and B sites is induced by nonmagnetic zinc substitution. The value of quadrupole splitting for A and B magnetic sites is very small in all the samples indicating that the local symmetry of the ferrites obtained is close to cubic.
Table 3: Mössbauer parameters for various compositions of ‘x’ in Rb$_{0.5-X/2}$Zn$_X$Mn$_{0.05}$Fe$_{2.45-X/2}$O$_4$ recorded at 300K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\delta^#$ mm/s</th>
<th>$\Delta$ mm/s</th>
<th>Magnetic hyperfine field Tesla</th>
<th>Distribution of Fe$^{3+}$ ions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0</td>
<td>0.31</td>
<td>0.006</td>
<td>50.47</td>
<td>48 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>0.01</td>
<td>48.76</td>
<td>52 (tet)</td>
</tr>
<tr>
<td>X=0.1</td>
<td>0.31</td>
<td>0.01</td>
<td>49.81</td>
<td>47 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>-0.06</td>
<td>43.76</td>
<td>49 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.44</td>
<td>------</td>
<td>04 (C.D.)</td>
</tr>
<tr>
<td>X=0.2</td>
<td>0.32</td>
<td>0.07</td>
<td>49.29</td>
<td>43 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>-0.03</td>
<td>42.91</td>
<td>44 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.37</td>
<td>------</td>
<td>13 (C.D.)</td>
</tr>
<tr>
<td>X=0.3</td>
<td>0.31</td>
<td>0.01</td>
<td>49.06</td>
<td>39 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>-0.05</td>
<td>42.66</td>
<td>40 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.34</td>
<td>------</td>
<td>23 (C.D.)</td>
</tr>
<tr>
<td>X=0.4</td>
<td>0.30</td>
<td>-0.05</td>
<td>48.78</td>
<td>35 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.10</td>
<td>41.81</td>
<td>31 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.21</td>
<td>------</td>
<td>34 (C.D.)</td>
</tr>
<tr>
<td>X=0.5</td>
<td>0.32</td>
<td>0.04</td>
<td>48.64</td>
<td>32 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.01</td>
<td>41.15</td>
<td>21 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.20</td>
<td>------</td>
<td>47 (C.D.)</td>
</tr>
</tbody>
</table>

$^\#$w.r.t. pure metallic iron absorber, oct.=octahedral site, tet.=tetrahedral site, C.D.=central doublet
Fig 17: Mössbauer spectrum for composition with $x = 0$

Fig 18: Mössbauer spectrum for composition with $x = 0.1$
Fig 19: Mössbauer spectrum for composition with x = 0.2

Fig 20: Mössbauer spectrum for composition with x = 0.3
Fig. 21: Mössbauer spectrum for composition with $x = 0.4$

Fig. 22: Mössbauer spectrum for composition with $x = 0.5$
Fig. 23: Variation in paramagnetic character with Zn content
4.2.2 Mixed cesium ferrites of composition $\text{Cs}_{0.5-X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$

4.2.2.1 XRD studies

Mixed cesium ferrites of various compositions i.e. $\text{Cs}_{0.5-X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$ were prepared by combustion method. Figure 24 shows the X-ray diffraction patterns for different compositions of $\text{Cs}_{0.5-X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$. The diffraction peaks reveal the existence of single phase cubic spinel ferrites and are comparable to those reported for respective rubidium ferrites. Figure 25 shows the variation of lattice constant (Table 4) as a function of ‘x’ which is attributed to the substitution of larger Zn$^{2+}$ cation (0.083nm) for smaller Fe$^{3+}$ cation (0.067 nm). Cesium ferrite being inverse spinel, have all the Cs$^+$ ions in octahedral position along with half of the Fe$^{3+}$ ions and remaining Fe$^{3+}$ ions occupy tetrahedral site. On addition of Zn$^{2+}$ ions which have strong affinity for tetrahedral site, only Fe$^{3+}$ ions present at tetrahedral site get replaced resulting in an increase in lattice parameter. The theoretical / X-ray density ($d_{\text{XRD}}$) and experimental densities (Figure 26) show a regular decrease with increasing ‘x’ value due to a decrease in molecular weight of the ferrite compositions. The average particle size of the ferrite product calculated from the XRD pattern comes out to be 15-20 nm. The size and shape of Cs-Zn ferrite particles synthesized by the solution combustion route were also analyzed by transmission electron micrographs (TEM). An average particle size of 18-22 nm has been estimated for the nanocrystalline $\text{Cs}_{0.5-X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$ powders as shown in Figures 27, 28. The smaller particle size may be attributed to the combustion synthesis involving molecular level heating without thermal gradient and requiring much smaller time than the conventional sintering ceramic technique. The elemental analysis of the different compositions has been carried out with the help of EDXRF technique (Figures 29, 30) and is found to be in agreement with the expected values within the instrumental error (±5%).
Table 4: Variation of various XRD parameters with composition ‘x’ for 
$\text{Cs}_{0.5-x/2}\text{Zn}_x\text{Mn}_{0.05}\text{Fe}_{2.45-x/2}\text{O}_4$.

<table>
<thead>
<tr>
<th>Composition (X)</th>
<th>Molecular weight</th>
<th>Density (d$_{\text{XRD}}$) g/cm$^3$</th>
<th>Density (d$_{\text{Exp}}$) g/cm$^3$</th>
<th>Porosity (%)</th>
<th>Lattice parameter ‘a’</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>270.45</td>
<td>6.0974</td>
<td>5.7019</td>
<td>6.45</td>
<td>8.3845</td>
</tr>
<tr>
<td>0.1</td>
<td>267.54</td>
<td>6.0180</td>
<td>5.6659</td>
<td>5.89</td>
<td>8.3909</td>
</tr>
<tr>
<td>0.2</td>
<td>264.63</td>
<td>5.9335</td>
<td>5.6158</td>
<td>5.35</td>
<td>8.3999</td>
</tr>
<tr>
<td>0.3</td>
<td>261.72</td>
<td>5.8477</td>
<td>5.5543</td>
<td>5.03</td>
<td>8.4097</td>
</tr>
<tr>
<td>0.4</td>
<td>258.51</td>
<td>5.7644</td>
<td>5.5298</td>
<td>4.06</td>
<td>8.4186</td>
</tr>
<tr>
<td>0.5</td>
<td>255.90</td>
<td>5.6698</td>
<td>5.4103</td>
<td>4.58</td>
<td>8.4333</td>
</tr>
</tbody>
</table>
Fig. 24: X-ray powder diffraction patterns for $\text{Cs}_{0.5-x/2}\text{Zn}_x\text{Mn}_{0.05}\text{Fe}_{2.45-x/2}\text{O}_4$ ($x = 0$ to 0.5)
Fig. 25: Variation of Lattice constant ‘a’ with Zn content.

Fig. 26: Variation of theoretical density (d_{XRD}) and experimental density (d_{Exp}) with Zn content (x).
Fig. 27: TEM micrograph for Cs_{0.5-x/2} Zn_x Mn_{0.05} Fe_{2.45-x/2} O_4 with x=0.1

Fig. 28: TEM micrograph for Cs_{0.5-x/2} Zn_x Mn_{0.05} Fe_{2.45-x/2} O_4 with x=0.5
Fig. 29: EDXRF graph for the composition with $x = 0.3$

Fig. 30: EDXRF graph for the composition with $x = 0.5$

4.2.2.2 Magnetic studies
Magnetic measurements reveal that all the samples show hysteresis loop, a typical ferrimagnetic behaviour of nanosized magnetic materials. **Figures 31 and 32** show the variation of saturation magnetization and Curie temperature as a function of Zn content. The magnetic parameters (**Table 5**) for mixed cesium ferrites show a similar trend to that observed for respective rubidium ferrites.

![Graph showing variation of saturation magnetization with Zn content](image)

**Fig.31: Variation of saturation magnetization with increasing value of ‘x’**
Fig. 32: Variation of Curie temperature with increasing value of ‘x’

Table 5: Variation of Saturation magnetization, Average particle size, Curie’s temperature and dc- resistivity with composition ‘x’ for Cs\textsubscript{0.5-X/2} Zn\textsubscript{X} Mn\textsubscript{0.05} Fe\textsubscript{2.45-X/2} O\textsubscript{4}

<table>
<thead>
<tr>
<th>Composition (X)</th>
<th>Saturation Magnetization Ms(emu/g)</th>
<th>Average particle size (XRD) (nm)</th>
<th>Curie’s temperature (°C)</th>
<th>Resistivity (Ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22</td>
<td>13.2</td>
<td>425</td>
<td>8.02*10\textsuperscript{3}</td>
</tr>
<tr>
<td>0.1</td>
<td>34</td>
<td>15.4</td>
<td>360</td>
<td>9.5*10\textsuperscript{7}</td>
</tr>
<tr>
<td>0.2</td>
<td>44</td>
<td>17.3</td>
<td>320</td>
<td>1.23*10\textsuperscript{6}</td>
</tr>
<tr>
<td>0.3</td>
<td>52</td>
<td>20.3</td>
<td>260</td>
<td>1.35*10\textsuperscript{6}</td>
</tr>
<tr>
<td>0.4</td>
<td>39</td>
<td>16.8</td>
<td>210</td>
<td>1.67*10\textsuperscript{6}</td>
</tr>
<tr>
<td>0.5</td>
<td>28</td>
<td>15.4</td>
<td>126</td>
<td>1.80 *10\textsuperscript{6}</td>
</tr>
</tbody>
</table>
4.2.2.3 Electrical studies

The electrical property in Cs-Zn ferrites has been attributed to electron hopping between the two valence states of iron, \( \text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} \), on octahedral sites. The \( \text{Fe}^{2+} \) ion concentration is a characteristic property of a given ferrite material and depends upon several factors such as sintering time, temperature and atmosphere, annealing time, etc., including the particle structure. The variation of room-temperature dc-resistivity as a function of composition is presented in Table 5. It shows a regular increase with Zn content as shown in Figure 33 and can be explained on the basis of Verwey mechanism of electron hopping between two valance states distributed randomly on equivalent lattice sites [27]. The temperature dependence of dc-resistivity was also studied in the temperature range 308-398 K as displayed in the Figure 34 that shows an almost linear decrease in resistivity with temperature suggesting semiconductor behaviour of the ferrite materials.

![Graph showing variation of dc resistivity with Zn content](image)

**Fig. 33: Variation of dc resistivity with Zn content**
Fig. 34: Temperature dependence of dc-resistivity for Cs$_{0.5-x/2}$Zn$_x$Mn$_{0.05}$Fe$_{2.45-x/2}$O$_4$ with composition $x = 0.1, 0.3, 0.5$
Dielectric properties for different ferrite samples were studied in the frequency range $10^3 - 10^7$ Hz, (Figure 35). The frequency dependence of the dielectric constant ($\varepsilon'$) shows a continuous decrease with increase in frequency with pronounced dispersion at lower frequency and it remains almost independent of applied external field at high frequency domain. The existence of dielectric dispersion can be explained on the basis of Koop’s two-layer model and Maxwell–Wagner polarization theory.

![Graph showing variation of dielectric constant with frequency for different compositions](image)

**Fig. 35: Variation of Dielectric constant for different compositions with frequency.**
Figure 36 shows an initial increase in the value of tangent loss (δ) to attain a maxima followed by a regular decrease with frequency. It can be noted that the height of the peak increases with Zn$^{2+}$ ions substitution at x=0.1, and then it shows a subsequent decrease with increase of Zn$^{2+}$ ion concentration. The decrease of the height of the peak of tan $\delta$ may be attributed to the substitution of diamagnetic Zn$^{2+}$ ions in place of Fe$^{3+}$ ions that limits the degree of conductivity by blocking hopping conduction mechanism, thus, resulting in an increase of resistivity.

Fig.36: Variation of Tangent loss (δ) for different compositions with frequency.
4.2.2.4 Mössbauer studies

Figures 37-42 show Mössbauer spectra for different compositions with x = 0 to 0.5 which are almost similar to those observed for respective mixed rubidium ferrites (Table 6). Mössbauer spectra show superimposition of a central paramagnetic doublet over the sextet pattern (x=0.1) and its intensity increases with further increase in Zn$^{2+}$ ion concentration as displayed in Figure 43, suggesting a transition from ferrimagnetic to super-paramagnetic phase with addition of diamagnetic zinc content (x).

![Mössbauer spectrum for composition with x = 0](image-url)
Fig. 38: Mössbauer spectrum for composition with $x = 0.1$

Fig. 39: Mössbauer spectrum for composition with $x = 0.2$
Fig. 40: Mössbauer spectrum for composition with x = 0.3

Fig. 41: Mössbauer spectrum for composition with x = 0.4
Fig. 42: Mössbauer spectrum for composition with $x = 0.5$

Fig. 43: Variation of paramagnetic character with Zn content
Table 6: Mössbauer parameters for various compositions of ‘x’ in $\text{Cs}_{0.5X/2}\text{Zn}_X\text{Mn}_{0.05}\text{Fe}_{2.45-X/2}\text{O}_4$ recorded at 300K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\delta^#$ mm/s</th>
<th>$\Delta$ mm/s</th>
<th>Magnetic hyperfine field (B) Tesla</th>
<th>Distribution of $\text{Fe}^{3+}$ ions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0</td>
<td>0.32</td>
<td>0.01</td>
<td>49.71</td>
<td>52 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>-0.008</td>
<td>46.76</td>
<td>48 (tet)</td>
</tr>
<tr>
<td>X=0.1</td>
<td>0.31</td>
<td>0.02</td>
<td>49.56</td>
<td>51 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>-0.01</td>
<td>46.24</td>
<td>46 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>0.63</td>
<td>------</td>
<td>03 (C.D.)</td>
</tr>
<tr>
<td>X=0.2</td>
<td>0.30</td>
<td>-0.001</td>
<td>49.38</td>
<td>46 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>-0.009</td>
<td>45.38</td>
<td>38 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.35</td>
<td>------</td>
<td>16 (C.D.)</td>
</tr>
<tr>
<td>X=0.3</td>
<td>0.31</td>
<td>0.04</td>
<td>49.31</td>
<td>44 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>-0.06</td>
<td>43.37</td>
<td>29 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.36</td>
<td>------</td>
<td>27 (C.D.)</td>
</tr>
<tr>
<td>X=0.4</td>
<td>0.30</td>
<td>-0.002</td>
<td>49.24</td>
<td>41 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.15</td>
<td>42.31</td>
<td>21 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.30</td>
<td>------</td>
<td>38 (C.D.)</td>
</tr>
<tr>
<td>X=0.5</td>
<td>0.30</td>
<td>-0.01</td>
<td>49.16</td>
<td>29 (oct)</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>-0.06</td>
<td>41.35</td>
<td>18 (tet)</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.34</td>
<td>------</td>
<td>53 (C.D.)</td>
</tr>
</tbody>
</table>

$^#$w.r.t. pure metallic iron absorber, oct.=octahedral site, tet.=tetrahedral site, C.D.=central doublet
4.3 Conclusions:

The following two series of mixed alkali metal ferrite materials have been synthesized by solution combustion method using stoichiometric aqueous solutions of respective metal nitrates and ethylene glycol.

\[
\begin{align*}
Rb_{0.5-X/2}Zn_XMn_{0.05}Fe_{2.45-X/2}O_4 \\
Cs_{0.5-X/2}Zn_XMn_{0.05}Fe_{2.45-X/2}O_4
\end{align*}
\]

Where ‘x’ varies from 0 to 0.5 in steps of 0.1.

Ethylene glycol acts as a fuel in the redox reaction involved in solution combustion method. By making use of this method, stoichiometrically pure ferrites have been obtained at lower temperature and in shorter time than the conventional ceramic method. Unlike the solid precursor thermolysis method employed for the preparation of ferrites, the solution phase combustion method is rapid and undergoes a direct conversion from the molecular mixture of the precursor solution to the final oxide product (ferrite), avoiding the formation of intermediate phases that require inter-diffusion for complete reaction.

X-ray powder diffraction studies reveal the formation of single phase spinel ferrites, which ensures the high purity of materials.

The lattice parameter ‘a’ has been found to increase with increasing Zn content (x) which is attributed to the larger cationic radii of substituent Zn\(^{2+}\) ions than Fe\(^{3+}\) ions being replaced.

An increase in the magnitude of saturation magnetization with increasing Zn content up to \(x = 0.3\) has been explained on the basis of Neel’s two sublattices model, while a decrease in the saturation magnetization with increasing Zn content for \(x > 0.3\) has been described on the basis of Yafet and Kittel spin canted structure.

The Curie temperature has been found to decrease with increasing Zn content (x) and is explained on the basis of exchange ion interactions.

In Mössbauer spectral studies, the Intensity of the doublet increases with increasing value of ‘x’ at the cost of sextets indicating a transition from ferrimagnetism to paramagnetism. The decrease in hyperfine fields at tetrahedral site with increasing Zn content (x) is attributed to the weakening of A-B exchange interactions due to the replacement of A site Fe\(^{3+}\) ions by non-magnetic Zn\(^{2+}\) ions.
Solution combustion method has several advantages over other conventional methods: (i) stoichiometrically pure ferrites with smaller size and greater surface area are obtained; (ii) ferrites are formed at lower temperature and in shorter time; (iii) evolution of gaseous products during decomposition dissipates the heat evolved and prevents sintering of the final product, thus facilitating the formation of nanoparticles. iv). 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.

Since the magnitude of Curie temperatures for Rb-Zn and Cs-Zn ferrites have been found to be higher than that of respective Na-Zn and K-Zn ferrites with same composition, mixed rubidium/cesium ferrites may be designated as the better option for application in magnetic/microwave devices.

The high dc-resistivity values obtained for the solution combustion route-processed Rb/Cs-Zn ferrites make them suitable for high-frequency applications. Apart from the academic interest involved, these investigations are of technological importance in the view of the fact that their end products (ferrites) play a key role as magnetic/engineering materials in the modern industry.
References
27. Verwey E., Haayman P. *Physica* 8 (1941) 979-999.