Lattice parameter variation and magnetization studies of titanium and zirconium substituted manganese-zinc ferrites

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The polycrystalline ferrites with the compositions $\text{Mn}_0.56\text{Zn}_{0.44}\text{Zr}_{0.02}\text{Fe}_{2.00}\text{O}_4$ and $\text{Mn}_0.56\text{Zn}_{0.44}\text{Zr}_{0.02}\text{Fe}_{2.00}\text{O}_4$ where $x = 0.0, 0.1, 0.2, 0.3$ and $0.4$ have been prepared. The variations in lattice parameter, saturation magnetization, Curie temperature and initial permeability are explained on the basis of the distribution of the dopant cations among the tetrahedral and octahedral sites of the ferrite lattice. Theoretically, evaluated lattice constant values are compared with the experimentally obtained lattice constant values and are in good agreement. The observations indicate the presence of non-collinear magnetic spin order on B sites. Magnetic moment and Yafet-Kittel angle values are also evaluated.

1 Introduction
Ferrite properties are very sensitive to additives/dopants while preparing the material\cite{1,2}. The lattice constant has been observed to increase with the addition of In ions while it decreased with Cr and Al dopants and magnetic properties also decreased with these dopants\cite{5}. The influence of the addition of Ge$^{4+}$ and Sn$^{4+}$ in Mn$_{0.56}$Z$_{0.44}$Fe$_{2.00}$O$_4$ has been studied earlier\cite{6}. The saturation magnetization ($M_s$) was found to have a peak value at 0.32 mol% of Ge, while core losses decreased passing through a minimum at the same mole composition. Initial permeability ($\mu_i$) and core losses were not affected significantly by the SnO$_2$ addition.

Titanium is known to lower the anisotropy field improving the microstructure of the lithium ferrite\cite{7} and it increases $\mu_i$ in Mg-Zn ferrite\cite{8}. Addition of Zr increased $T_c$ in Li-Zn ferrite\cite{9} while it improved $T_c$, $h_{10}$ and $H_{10}$ in the Cu-Zn ferrite\cite{10}. In the light of the above improvements of the magnetic properties, since the Mn-Zn ferrites are important core materials for the application up to several MH$\mu$, Ti and Zr were chosen as the dopants for the present studies in Mn-Zn ferrite. Hence, the influence of titanium or zirconium ions in Mn-Zn ferrites on the lattice constant, saturation magnetization, Curie temperature and initial permeability is studied. These are explained on the basis of dopant cation distribution among tetrahedral and octahedral sites and consequent changes in the magnetic interactions.

2 Experimental Details
Ferrites with the composition $\text{Mn}_0.56\text{Zn}_{0.44}\text{M}_x\text{Fe}_{2.00}\text{O}_4$ (where $M = \text{Zr}^{4+} / \text{Ti}^{4+}$ and $x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) were prepared by a conventional ceramic technique. The sintering was done at 1200$^\circ$C in air for 2 hrs and cooled in the furnace to room temperature. Single phase formation of cubic spinel structure was confirmed by X-ray diffractograms. The present measurements of the Curie temperature ($T_c$) were made by the Latora-Sinha technique\cite{11} and the saturation magnetization ($M_s$) by the pendulum (ponderometer) method was described by Rathenau and Snook\cite{12}. The initial permeability was obtained with the technique explained by Heck\cite{13}.

3 Results and Discussion
3.1 Lattice parameter and proposal of possible cation distribution
Lattice parameter $(a)$ values are given in Table 1. The lattice constant is found to increase with both the dopant concentration $(x)$ except at $x = 0.1$ of Zr substitution where it has a minimum (8.434 Å). The value of the lattice constant obtained for the basic ferrite (8.519 Å) is in good agreement with the reported\cite{15} value 8.498 Å. Theoretically, the lattice constant value can be evaluated...
with the known cation distribution of a ferrite and the detailed procedure was reported earlier\(^1\). The cation distribution for the present basic/undoped ferrite can be written as \((\text{Zn}^{2+} \text{Mn}^{2+} \text{Fe}^{3+} \text{Fe}^{2+} \text{O}_2\text{O}_4\)), which was reported earlier\(^1\). In the present studies, taking the cation distribution mentioned above for the undoped ferrite, theoretical \(a\) value is evaluated. The theoretically evaluated \(a\) is close to the experimentally obtained \(a\) value of the basic Mn-Zn ferrite. In the present Mn-Zn system, Mn-Zn \(\text{Fe}_2\text{O}_4\) series of ferrites, variation of tetravalent \(\text{Zr}/\text{Ti}\) concentration results in the replacement of \(2 \times \text{Fe}^{3+}\) ions by \(x\text{M}^{4+}\) ions, \((x/2)\text{Mn}^{2+}\) and \((x/2)\text{Zn}^{2+}\) ions. It was reported that \(\text{Ti}^{4+}\) ions occupy only the octahedral (B) sites\(^1\). Small amount of \(\text{Zr}^{4+}\) ions favour to occupy A sites\(^4\). Based on these earlier studies\(^1,4\) and comparing the site preference energies of the constituent ions\(^4\), the cation distribution formulae have been proposed for all the present ferrite materials studied. For the present Zr doped ferrites the proposed cation distribution at \(x = 0.00\) is \((Zn_{0.97+x}\text{Zr}_{0.03}Mn_{0.54+x}\text{Fe}^{3+}_{0.05}\text{Zr}_{0.45-x}\text{Fe}^{2+}_{0.05}\text{Zr}_{0.55-x}\text{Fe}^{2+}_{0.05}\text{O}_2\text{O}_4\)) for Ti doped ferrites it is \((Zn_{0.97+x}Mn_{0.54+x}\text{Fe}^{3+}_{0.05}Zr_{0.45-x}\text{Fe}^{2+}_{0.05}\text{Zr}_{0.55-x}\text{Fe}^{2+}_{0.05}\text{Ti}_{0.45-x}\text{Fe}^{2+}_{0.05}\text{Fe}_{0.45-x}\text{O}_2\text{O}_4\)) where \(k\) value is 0.05 and constant for all values of \(x\), but if \(x\) value is zero then \(k\) value also zero. With these distribution theoretically lattice constants are computed using the above mentioned procedure\(^1\). These are compared with the experimentally obtained \(a\) values, found reasonable agreement between them and are given in Table 1 along with the cation distribution for each concentration of dopant. The % error is attributed to the porosity and cation vacancies formed during sintering. Substitution of high valence cations in the matrix of ferrites under oxidizing conditions is expected to produce cation vacancies\(^1\). The influence of these vacancies is not taken into consideration for the theoretical evaluation of \(a\) values. In order to substantiate the above proposed cation distribution, theoretically XRD intensities are calculated using the formula given by Burger\(^6\) as done for Co-Si ferrite series by Shinde \textit{et al}\(^1\). To estimate the constituent cations concentrations at tetrahedral (A) and octahedral (B) sites in the present ferrite series, the ratio of X-ray diffraction lines \(I_{200}/I_{110}\) and \(I_{400}/I_{422}\) have also been evaluated from the presently observed X-ray diffractograms. Earlier studies of Co-Si ferrites reported\(^1\) that the agreement and disagreement between observed and calculated values of \(I_{200}/I_{110}\) and \(I_{400}/I_{422}\) were due to collinear spin ordering and non-collinear spin ordering respectively. For the present undoped Mn-Zn ferrite existence of significant canting and non-collinear magnetic structure was reported earlier\(^1\). In the present studies, the observed intensity ratio values of X-ray diffractograms are compared with the same obtained from the theoretical results of the X-ray intensity calculations and found disagreement between them substantiating earlier results i.e., existence of non-collinear spin ordering and results are given in Table 2. However, usually XRD intensities are not sensitive to magnetic ordering in the crystals. Hence, in this context the phenomenon relating to the decrease of the X-ray intensity ratio as the magnetic ordering of the system becomes non-collinear is unclear. Thus, at present it is some what difficult to understand the effect of the XRD intensities on the magnetic ordering. These calculation lead to the conclusion that the preferential sites for Ti are octahedral (B) and for Zr both tetrahedral (A) and octahedral (B). In the study of effect of Ge and Sn doped Mn-Zn ferrite\(^3\), the lattice constant \(a\) was found to increase continuously with Sn dopant concentration up to 5 mol%. Doping with Ge caused slight decrease in the lattice constant from the value of undoped ferrite. The

<table>
<thead>
<tr>
<th>Cation distribution</th>
<th>(X)</th>
<th>(A_{cal})</th>
<th>(A_{exp})</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>((Zn_{0.37}Mn_{0.63}Fe^{3+}_{0.05}))</td>
<td>0.0</td>
<td>8.484</td>
<td>8.519</td>
<td>0.41</td>
</tr>
<tr>
<td>((Zn_{0.42}Mn_{0.58}Fe^{3+}_{0.05}))</td>
<td>0.1</td>
<td>8.711</td>
<td>8.434</td>
<td>3.21</td>
</tr>
<tr>
<td>((Zn_{0.47}Mn_{0.53}Fe^{3+}<em>{0.05}Mn</em>{0.15}))</td>
<td>0.2</td>
<td>8.752</td>
<td>8.535</td>
<td>2.55</td>
</tr>
<tr>
<td>((Zn_{0.52}Mn_{0.48}Zn_{0.05}))</td>
<td>0.3</td>
<td>8.793</td>
<td>8.544</td>
<td>2.92</td>
</tr>
<tr>
<td>((Zn_{0.57}Mn_{0.43}Zn_{0.05}))</td>
<td>0.4</td>
<td>8.833</td>
<td>8.545</td>
<td>3.38</td>
</tr>
<tr>
<td>((Zn_{0.62}Mn_{0.38}))</td>
<td>0.5</td>
<td>8.606</td>
<td>8.520</td>
<td>1.10</td>
</tr>
<tr>
<td>((Zn_{0.42}Mn_{0.58}))</td>
<td>0.6</td>
<td>8.718</td>
<td>8.529</td>
<td>2.21</td>
</tr>
<tr>
<td>((Zn_{0.47}Mn_{0.53}))</td>
<td>0.7</td>
<td>8.613</td>
<td>8.542</td>
<td>1.04</td>
</tr>
<tr>
<td>((Zn_{0.52}Mn_{0.48}))</td>
<td>0.8</td>
<td>8.639</td>
<td>8.556</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 1 — Proposed cation distribution, calculated and observed lattice parameter\((a)\) values for the system Mn_{0.58+x}Zr_{x}Sn_{x}Fe_{2-x}Zr_{1-x}O_{4} M = Zr/\text{Ti}
increase in the $a$ with Ge addition was explained on the basis of small ionic radius of Ge (0.44 Å) comparative to the ions in the host ferrite. It was expected to dissolve to a very limited extent by occupying A sites only, where as Sn$^{4+}$ cation with ionic radius 0.69 Å goes into solid solution with the ferrite.

Further, the variation of magnetic properties like $M_s$ and $T_c$ in Zr$^{4+}$, Sn$^{4+}$, Nb$^{5+}$ and Ti$^{4+}$ substituted Ni-Zn ferrites was explained on the basis of these ions, first entering the A sites and later going to the B sites at higher concentration. Similarly a sharp drop of $M_s$ in these Ni-Zn ferrites followed by rise was explained on the assumption that Ti$^{4+}$ dopant ions going to A sites first up to a particular concentration and subsequently moving to both A and B sites. The lattice parameter was decreased with the concentration for all the dopants except for Ti$^{4+}$ substitution in which it had an initial fall and rise later. The variation of lattice parameter due to Zr and Ti substitution was explained by the combined effect of cation size on $b$ the repulsion parameter and of the A site charge on $M_s$, the Madelung constant since the lattice parameter is proportional to $(b/M)$.

In the present studies the initial fall of $a$ for Zr substituted ferrites is explained by considering the influence of Zr$^{4+}$ on $(b/M)$. For high valence cations like Zr$^{4+}$ when they occupy A sites, the A site charge increases and hence $M_s$, the Madelung constant since this is proportional to A site charge. The increase of the $b$ value is offset by increasing $M_s$ value. Hence, the lattice parameter decreases. The entrance of non-magnetic cation(s) like Zr$^{4+}$ into A sites reduces the magnetization of A sublattice and thus the net magnetization increases. This is reflected in the saturation magnetization values also where initially it rises. From $x = 0.2$, Zr$^{4+}$ cation size (0.80 Å) and Ti$^{4+}$ size (0.64 Å) (for all the $x$ values of Ti)

<table>
<thead>
<tr>
<th>X</th>
<th>I_{250400}</th>
<th>I_{1204000}</th>
<th>I_{40422}</th>
<th>I_{40422}</th>
<th>I_{106000}</th>
<th>I_{106000}</th>
<th>I_{108022}</th>
<th>I_{108022}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc</td>
<td>Zr</td>
<td>Zr</td>
<td>Zr</td>
<td>Zr</td>
<td>Ti</td>
<td>Ti</td>
<td>Ti</td>
<td>Ti</td>
</tr>
<tr>
<td>0.0</td>
<td>0.98</td>
<td>0.85</td>
<td>1.72</td>
<td>1.57</td>
<td>0.98</td>
<td>0.85</td>
<td>1.72</td>
<td>1.57</td>
</tr>
<tr>
<td>0.1</td>
<td>0.84</td>
<td>0.59</td>
<td>1.86</td>
<td>0.94</td>
<td>0.78</td>
<td>0.47</td>
<td>1.91</td>
<td>0.89</td>
</tr>
<tr>
<td>0.2</td>
<td>0.77</td>
<td>0.42</td>
<td>1.94</td>
<td>0.69</td>
<td>0.61</td>
<td>0.36</td>
<td>2.09</td>
<td>0.76</td>
</tr>
<tr>
<td>0.3</td>
<td>0.65</td>
<td>0.34</td>
<td>2.08</td>
<td>0.76</td>
<td>0.41</td>
<td>0.24</td>
<td>2.21</td>
<td>0.64</td>
</tr>
<tr>
<td>0.4</td>
<td>0.60</td>
<td>0.31</td>
<td>2.17</td>
<td>0.80</td>
<td>0.33</td>
<td>0.16</td>
<td>2.32</td>
<td>0.61</td>
</tr>
</tbody>
</table>

come into prominence resulting in an increase of $b$, the repulsion parameter and hence $a$ when these enter B sites. During the preparation of samples, the dopants were substituted at the expense of Fe$^{3+}$ cations (0.64 Å) and their cation size as given above is greater than Fe$^{3+}$ size.

3.2 Variation of magnetic properties

The variation of saturation magnetization ($M_s$) and Curie temperature ($T_c$) is shown in the Figs 1 and 2 respectively. With the Ti substitution, $M_s$ and $T_c$ are found to decrease with the concentration. To know more about magnetic structure of the present ferrites, magnetic moment values (observed and theory) are evaluated. From the observed $M_s$ values, the observed magnetic moment($n_{obs}$) values are evaluated using the equation

$$n_{obs} = (M_s/d)(M/5585)$$

where $M_s$ is the saturation magnetization, $d$, experimental density and $M$ is the molecular weight of the ferrite.
According to the Neél's two sublattice model of ferrimagnetism, theoretical magnetic moments can be calculated by the relation

$$n_B^{(\text{Neel})} = M_B - M_A \quad \ldots (2)$$

$M_B$ and $M_A$ are the B and A sublattice magnetic moments respectively. In the present studies for $x = 0.0$ to 0.4, $n_B$ values are calculated using ionic magnetic moments of Fe$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Zr$^{4+}$ and Ti$^{4+}$. Since these values are valid at 0K, these cannot be compared with the observed values of $n_B$ which valid for 300 K. However, the observed relative magnetic moments such as $[n_B(x)_{\text{obsd}}]/[n_B(0)_{\text{obsd}}]$ at 300 K are compared with the theoretical (Neél’s model) relative magnetic moment $[n_B(x)_{\text{Neel}}]/[n_B(0)_{\text{Neel}}]$ values and are summarized in Table 3. In the earlier studies, agreement between the observed and theoretical relative magnetic moment values was found confirming the collinear spin ordering and disagreement also found indicating the non-collinear order. The present discrepancy between observed and theoretical $n_B$ values can be understood in terms of significant non-collinear behaviour as already mentioned in the section 3.1 that the present undoped ferrite was reported to be non-collinear.

In the present studies, discrepancy between observed and theoretical $n_B$ values are increased with the dopant concentration ($x$). With the increase of $x$, the increased discrepancy of relative $n_B$ values suggest the dominant role of canted spin (non-collinear) on B sites existing Yafet-Kittel angles having strong influence on the $M_s$ variation with $x$. The observed cantiing angles ($\alpha_{B}$) have been obtained from the observed $n_B$ variation with $x$ by the relation

$$n_B(x)_{\text{obsd}} = M_B(x)\cos \alpha_{B} + M_A(x) \quad \ldots (3)$$

These values are also given in Table 3. Thus the observed $M_s$ variation has been explained on the basis of Yafet-Kittel angles existence on the B site spin besides two sublattice models. Ti$^{4+}$ ions going into B sites decrease the magnetic moment of the B sublattice and also modify the exchange interactions of A and B sites. Hence, the net magnetization, $M_s$ decreases. In the case of Zr substitution as explained in the lattice parameter variation, these ions enter A sites up to the concentration of $x = 0.1$. This decreases the A sublattice magnetization and thereby increasing net magnetization, $M_s = M_A - M_B$ (Zr$^{4+}$ being nonmagnetic). For further increase in the concentration, Zr$^{4+}$ ions enter both A and B sites causing reduction in both $M_A$ and $M_B$. Hence the $M_s$ continuously decreases up to the concentration studied i.e. 0.4. Thus these studies indicate the modification of A-B and B-B exchange interactions. However, studies using Moss-
The ferrimagnetic Curie temperature is for further concentrations of Neel’s two sublattice model and canting spin on B concentration. Except at substituted ferrite a similar behaviour can account for $X = (M_A + M_B)IB$.

From the present studies it is concluded that the Zr$^{4+}$ ions initially enter A sites up to a concentration of $x = 0.1$ and later enter both A and B sites in the mixed ferrite $M_{0.58}Zr_{0.37}Fe_{2.05}O_4$, whereas Ti$^{4+}$ ions enter B sites only. The variation of lattice parameter is explained on the basis of dopant cation size compared to the host ion size and changes in the value of Madelung constant. The experimental values of lattice parameter are in good agreement with the theoretically obtained values. The variation in $M_s$ and $T_c$ are explained for Zr/Ti substitution taking into account the modification of A-B and B-B exchange interactions and Curie constants. Magnetic moment and Yafet-Kittel angle values are evaluated. With the increase of dopant concentration, contribution of non-collinear magnetic spin order is more. Based on experimental data cation distributions are proposed.

References