Controlling the properties of Mn-Zn ferrites at high frequency by substituting In$^{3+}$ and Al$^{3+}$ ions

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The effect of substitution of In$^{3+}$ and Al$^{3+}$ ions on the electrical and magnetic properties of Mn-Zn spinel ferrites has been investigated. The substitution of In$^{3+}$ ions in place of Fe$^{3+}$ ions resulted in an increase of lattice parameter, because of the larger size of the substituted ions, whereas lattice parameter decreased on substituting Al$^{3+}$ ions in place of the Fe$^{3+}$ ions, owing to their smaller size. The dc resistivity was found to increase with the substitution of In$^{3+}$ and Al$^{3+}$ ions in the Mn-Zn ferrite system. The improvement in the dc resistivity has been observed at the expense of deterioration in the magnetic properties of Al$^{3+}$ substituted Mn-Zn Ferrites. A significant reduction in the value of initial permeability, saturation magnetization and Curie temperature was observed with successive increase of Al$^{3+}$ ions. The saturation magnetization and initial permeability were found to increase with incorporation of In$^{3+}$ ions. A marked increase in the value of initial permeability was found for the Mn$_{0.4}$Zn$_{0.6}$In$_{0.5}$Fe$_{1.5}$O$_4$ ferrites. The Curie temperature was found to decrease with an increase of In$^{3+}$ ion concentration. Possible mechanisms contributing to these processes have been discussed.

Keywords: Mn-Zn ferrite, Lattice parameter, Saturation magnetization, Curie temperature

1 Introduction

Replacing some of the Fe$^{3+}$ ions in the ferrites with spinel structure by In$^{3+}$ and Al$^{3+}$ ions alter the magnetic and electrical properties of the ferrites. The Mn-Zn ferrites are quite versatile from the point of view of their applications and simplicity of their preparation. These ferrites have a rectangular hysteresis loop characteristics, making them highly suitable for use in memory, cores of transformers, ferrofluids, permanent magnets, switching circuits of digital computers, as phase shifter and in several other applications. In our earlier work, we have studied structural, electrical and magnetic properties of mixed Mn-Zn ferrites up to 13 MHz frequency of applied ac field. In the present paper, the effect on the structural, electrical and magnetic properties of the system of ferrites Mn$_{0.4}$Zn$_{0.6}$M$_x$Fe$_{2-x}$O$_4$ by incorporating trivalent ions (M = Al$^{3+}$ and In$^{3+}$), into the matrix of the Mn-Zn ferrites has been investigated. The value of x was varied from 0 to 0.5 in steps of 0.1 in the Mn-Zn ferrite system. The frequency of ac field is set at 30MHz.

2 Experimental Details

The spinel ferrite series with the composition Mn$_{0.4}$Zn$_{0.6}$M$_x$Fe$_{2-x}$O$_4$, in which x was varied from 0.0 to 0.5 in steps of 0.1 were prepared using the standard ceramic technique. Analytical grade reagents ZnO (>98%, Merck, India), MnO (>98%, Merck, India), In$_2$O$_3$, (>98.5%, Merck, India), Al$_2$O$_3$ (>98.5%, Merck, Germany) and Fe$_2$O$_3$ (>98%, Merck, India) were weighed in proper proportions and thoroughly mixed by wet blending with distilled water in an agate mortar and pestle. The mixed powder was calcinated at 1000°C for 3 hr in a platinum crucible to improve the homogeneity of the constituents. The reacted material was well milled to reduce the particle size, after adding a small quantity of polyvinyl alcohol. The pulverized powder was granulated through sieves of mesh size 85-120 (BSS) and compressed to form pellets and torroids. These samples were finally sintered at 1300°C for 3 hr in air at the rate of 100°C /hr and subsequently cooled to room temperature by switching off the power supply of the furnace.

The X-ray diffraction (XRD) measurements were taken on a Rigaku Geiger Flex 3 kW diffractometer using CuK$_alpha$ source ($\lambda = 1.54\text{\AA}$) with Siemen X-ray diffractometer (D 5000). Scanning electron micrographs (SEM) were recorded using JEOL-7400 FEG-SEM and EDS (capable of 1nm resolution) at the University of Dundee, U K. The dc resistivity of the samples was measured at room temperature by the two terminal dc method, using spring loaded copper
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Electrodes connected to a Keithley electrometer, model 610C. The dielectric constant and initial permeability were measured by using Agilent Technologies 4285A Precision LCR Meter (upto 30 MHz). The saturation magnetizations of the samples were determined using a Vibrating Sample Magnetometer model EC and G 155. The X-ray diffraction studies of the prepared samples were also made to confirm their structure and determine other related properties. The Curie temperature was measured by using gravity separation method.

3 Results and Discussion

Fig. 1 shows X-ray diffraction pattern of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ ferrite and the position and relative intensities of the various X-ray diffraction peaks. The diffraction pattern shows the characteristic lines of spinel structure ferrite. No extra line is observed, which indicates that the sample have single phase spinel structure. Fig. 2 shows the scanning electron micrograph of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ ferrite sample which indicates that the sample has almost uniform sized crystallites with uniform grain growth. The average grain size is calculated by using Scherrer’s formula and is found to be about 0.89μm, which is found to be in good agreement with SEM. Lattice parameter, $dc$ resistivity and Curie temperature of mother sample are found to be 8.393Å, 6.6 x 10$^6$Ωcm and 477K, respectively.

The X-ray diffraction studies of various compositions of Mn$_{0.4}$Zn$_{0.6}$M$_x$Fe$_{2-x}$O$_4$ ferrites are used to obtain the lattice parameter, which is found to increase with increase in the value of $x$ on substitution with In$^{3+}$ ions as shown in Table 1. Such a change in the lattice parameter is expected. The Fe$^{3+}$ ions, which are of smaller radius (0.067 nm), are being replaced with increasing amount of In$^{3+}$ ions, which are of larger size (0.091 nm). In case of substitution by the Al$^{3+}$ ions, the lattice parameter was found to decrease linearly with increasing concentration of the substituted ions. Such a change in the lattice parameter was also expected. The ionic radius of the Al$^{3+}$ ions is 0.051 nm, which is smaller than the ionic radius (0.067 nm) of the Fe$^{3+}$ ions, which these substituting ions replace.

So, there is an expansion of the unit cell in case of the

<table>
<thead>
<tr>
<th>$x$</th>
<th>Lattice constant (Å)</th>
<th>$dc$ resistivity ($x 10^6$Ωcm)</th>
<th>Average grain size (μm)</th>
<th>Curie temperature (K)</th>
</tr>
</thead>
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<tr>
<td>In$^{3+}$</td>
<td>Al$^{3+}$</td>
<td>In$^{3+}$</td>
<td>Al$^{3+}$</td>
<td>In$^{3+}$</td>
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</tr>
<tr>
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<td>8.571</td>
<td>8.322</td>
<td>10.84</td>
<td>9.48</td>
</tr>
</tbody>
</table>

Fig. 1—XRD of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ sintered at 1300°C for 3 hr

Fig. 2—Scanning electronmicrograph (SEM) of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ ferrites sintered at 1300°C for 3 hr Mn$_{0.4}$Zn$_{0.6}$In$_x$Fe$_{2-x}$O$_4$ ferrites, whereas a shrinkage of
The dc resistivity is found to increase for all values of \( x \), in both the series as shown in Table 1 which can be explained on the basis of the Verwey’s hopping mechanism\(^{11}\). According to it, the electrical conduction in ferrites results from a hopping of the electrons between the ions of the same element, but of different valence state present at the octahedral or the B-site. The conduction in the \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{O}_{4} \) ferrite results mainly from the hopping between the \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions present at the B-sites\(^{12}\). Besides this, the presence of \( \text{Mn}^{3+} \) ions, if any, at the B-site may also initiate hopping between the \( \text{Mn}^{2+} \) and \( \text{Mn}^{3+} \) ions and may thus make a small contribution to the conductivity. The occurrence of a small percentage of \( \text{Fe}^{2+} \) and \( \text{Mn}^{3+} \) ions in these ferrites may result from either sintering process\(^{13}\) or electron exchange between \( \text{Mn}^{2+} \) and \( \text{Fe}^{3+} \) ions, as given by:

\[
\text{Mn}^{2+} + \text{Fe}^{3+} \rightarrow \text{Mn}^{3+} + \text{Fe}^{2+} \quad \ldots (1)
\]

Since both the \( \text{Fe}^{2+} \) and \( \text{Mn}^{3+} \) ions have a strong preference for occupying the B-sites\(^{14}\), they readily participate in the conduction process. The substituted \( \text{Al}^{3+} \) ions in the basic ferrite \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2}\text{O}_{4} \) ferrite, do not participate in hopping, although they have a preference for the B-sites\(^{15}\). They displace equal number of \( \text{Fe}^{3+} \) ions from the B sites, thus, increasing the resistivity\(^{16}\).

The substitution of \( \text{In}^{3+} \) for \( \text{Fe}^{3+} \) ions in the \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2}\text{O}_{4} \) ferrite has a similar effect on the resistivity, except that the \( \text{In}^{3+} \) ions, besides occupying the B sites, also have a tendency to occupy the A sites, thus, displacing an equal number of \( \text{Fe}^{3+} \) ions to the B sites, which increases the resistivity, but at a slow rate. The sharp increase in the resistivity on substitution of \( \text{Al}^{3+} \) ions in the \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2}\text{O}_{4} \) ferrites can be explained by taking into account the dilution effect\(^{17}\) of \( \text{Al}^{3+} \), due to which the increased concentration of \( \text{Al}^{3+} \) ions inhibit the \( 2\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-} \) conduction process. The X-ray diffraction studies indicate that all the samples have a single phase spinel structure, and segregation of the dopants, if any, is expected to be small. So the effect of grain boundary segregation on the resistivity of the \( \text{Mn-Zn-M} \) series of ferrites with increasing concentration of the Al or In-ions is expected to be minimal even in the dopant rich phases.

The introduction of \( \text{Al}^{3+} \) ions into the octahedral sub-lattice of \( \text{Mn-Zn ferrite} \) causes a decrease in the saturation magnetization \( 4\pi M_s \) (Fig. 3.). The greatest decrease in the in the value of \( 4\pi M_s \) occurs when the \( \text{Fe}^{3+} \) ions are replaced by the \( \text{Al}^{3+} \) ions in the \( \text{Mn-Zn ferrite} \). Incorporation of the \( \text{In}^{3+} \) ions into the \( \text{Mn-Zn ferrite} \) matrix for \( 0<x<0.3 \) leads to a rise in the saturation magnetization to a maximum, but there is a decrease beyond \( x = 0.3 \) as shown in Fig. 3. The rise in the \( 4\pi M_s \) value is attributed to the fact that incorporation of indium ions into the A sub-lattice leads to a rise in magnetic moment of the B sub-lattice with only a slight decrease in the magnetic moment of the A sub-lattice so that the total magnetic moment increases. Any further increase in the number of the indium ions in ferrite beyond \( x = 0.3 \), weakens the negative A-B interaction, because the \( \text{In}^{3+} \) (A)—\( \text{Fe}^{3+} \) (B) interaction is weaker than the \( \text{Fe}^{3+} \) (A)—\( \text{Fe}^{3+} \) (B) interaction. So, it results in the reduction of the resultant magnetization, as \( x \) exceeds 0.3.

The Curie temperature decreases almost linearly with the increased substitution of \( \text{In}^{3+} \) and \( \text{Al}^{3+} \) ions, as shown in Table1. This decrease can be explained on the basis of the number of magnetic ions present in the two sub-lattices and their mutual interactions. As
the concentration of In$^{3+}$ ions increases at the tetrahedral site, the replaced Fe$^{3+}$ ions go to the octahedral site. This leads to a decrease in the A-B interaction of the type Fe$^{3+}$(A)-O$_2$-Fe$^{3+}$(B). Since Curie temperature is determined by an overall strength of the A-B exchange interaction, the weakening of the Fe$^{3+}$(A)-O$_2$-Fe$^{3+}$(B) interaction results in a decrease of the Curie temperature$^{17}$, when the concentration of the In$^{3+}$ increases successively in the Mn-Zn-In ferrites.

In the case of Al$^{3+}$ substituted ferrite series, the Fe$^{3+}$ ions are being replaced by the substituted ions at B-site. Since the magnetic moment of the Al$^{3+}$ ions is zero, whereas the magnetic moment of Fe$^{3+}$ ions is 5.0 $\mu_B$, an increase in the concentration of the Al$^{3+}$ ions results in a reduction of the density$^{9,17}$ of the magnetic ions. This results in a reduction of the density of the net magnetic moment at the B-sublattice, weakening the A-B exchange interaction and thus, decreasing the Curie temperature. The variations of initial permeability, $\mu_i$, with $x$ for In$^{3+}$ and Al$^{3+}$ are shown in Fig.5 which indicates that an increase in $\mu_i$ when the amount of In$^{3+}$ ions is increased up to 0.5 in Mn$_{0.4}$Zn$_{0.6}$ In$_x$Fe$_{2-x}$O$_4$ ferrites. It yields a marked increase in the initial permeability up to a high value of 12410 for Mn$_{0.4}$Zn$_{0.6}$Al$_{0.5}$Fe$_{1.5}$O$_4$ ferrites. The initial permeability, $\mu_i$, decreases when the amount of Al$^{3+}$ ions is increased up to 0.5 in the Mn$_{0.4}$Zn$_{0.6}$Al$_x$Fe$_{2-x}$O$_4$ ferrites. These variations$^{18}$ can be explained from the following dependence of $\mu_i$:

$$\mu_i \propto M^2 D_m / K_1$$  \hspace{1cm} (2)

where $D_m$ is the average grain diameter, $K_1$ is the magneto-crystalline anisotropy constant and $M_i$ is the saturation magnetization. It has been observed that the average grain diameter $D_m$ changes insignificantly due to substitution of the In$^{3+}$ and Al$^{3+}$ ions in the Mn-Zn ferrite. As $\mu_i$ is proportional to $M_i^2$, the variation with $x$ for In$^{3+}$ and Al$^{3+}$ should be affected in a manner similar to that of variation of $M_i^2$ with which can be obtained from Fig.3. Fig.6 shows $\mu_i$ variation of the In$^{3+}$ doped samples with $M_i^2$ with error bar of 5%. In the curve, the values of $\mu_i$ have been normalized with respect to the value of $\mu_i$ at $x = 0$. From this graph, it seems the variations of $\mu_i$ with In$^{3+}$ ion concentration show a large change than produced by $M_i^2$ alone. This implies that apart from the variations of $M_i$, the magneto-crystalline-anisotropy constant $K_i$ does play an important role in changing the value of initial permeability, $\mu_i$, with increase in the concentration of In$^{3+}$ ions. The variations of $K_i$ can be qualitatively explained on the basis of single ion anisotropy model, which shows that Fe$^{3+}$ ions present at the A as well as B sites contribute to the anisotropy energy. The net value of $K_i$ is given by the relative contribution of the positive anisotropy of Fe$^{3+}$ ions at the tetrahedral site, which is compensated by the negative anisotropy of Fe$^{3+}$ ions at the octahedral site$^{17}$. As the concentration of the In$^{3+}$ ions is increased the cation distribution of Fe$^{3+}$ ions become modified$^9$ and yields a different number of Fe$^{3+}$ ions present at both the sites, which in turn affects $K_i$. Although the Fe$^{2+}$ ions are inevitably formed during the sintering process, yet they are not contributing significantly to the anisotropy energy in

![Fig. 4—Variation of initial permeability, $\mu$ at 30 MHz with $x$ Mn$_{0.4}$Zn$_{0.6}$M$_x$Fe$_{2-x}$O$_4$ ferrites](image-url)
our samples. This is due to the fact that the resistivity of all our samples is very high, leading to the conclusion that the concentration of Fe$^{2+}$ ions is very small. The anisotropy constant $K_1$ for the Fe$^{2+}$ ions is positive, and its contribution to the permeability is very small and appears to remain constant. Therefore, its contribution can be neglected. This implies that the net anisotropy constant $K_1$ is reduced to its minimum value when the concentration of the In$^{3+}$ ions, $x = 0.519$. This in turn yields a marked increase in the maximum value of $\mu_i$ at $x = 0.5$.

The variation of values of initial permeability, $\mu_i$, as function of the concentration $x$ of the Al$^{3+}$ and In$^{3+}$ ions, is shown in Fig.4. It shows a continuous decrease in the value of initial permeability with the increasing concentration of the Al$^{3+}$ ions. These variations can also be explained on the basis of Eq.(2). The variation of $\mu_i$ with concentration of Al$^{3+}$ ions is affected in a manner similar to those of variations of $M_s^2$ with concentration $x$ of the Al$^{3+}$ and can be obtained from Fig.3. In this series of ferrites also, the magneto-crystalline-anisotropy constant $K_1$, plays an important role in the variation of $\mu_i$ with $x$ the concentration of the substituted ions Al$^{3+}$. The constant $K_1$ continuously increases with addition of Al$^{3+}$ ions leading to a reduction in the value of $\mu_i$. According to Brion and Nemback, the soluble non-magnetic impurities inside the grain, hinder the reversible motion of domain walls. The motion of domain walls can be effective only when these form a continuous system and lower the initial permeability. The addition of soluble non-magnetic impurity also results in an increase of anisotropy energy and hence, reduces $\mu_i$. Since, it is not possible to find the inclusions and their distribution inside the grains, no quantitative arguments can be given to describe their effect on $\mu_i$. However, the above mentioned arguments qualitatively explain the effect of substituted ions on the value of $\mu_i$.

4 Conclusion

Mixed Mn-Zn spinel ferrites have been synthesized by conventional ceramic technique. It is concluded from the present study that amongst various compositions of Mn-Zn-Al ferrites, Mn$_{0.4}$Zn$_{0.6}$In$_{0.5}$Fe$_{1.5}$O$_4$ ferrite yields superior microstructural, electrical and magnetic properties. In the case of the Mn-Zn-Al ferrites, the electrical properties are even superior to those of Mn$_{0.4}$Zn$_{0.6}$In$_{0.5}$Fe$_{1.5}$O$_4$ ferrite, but the magnetic properties of these ferrites deteriorate. These optimized samples can be successfully used for high frequency applications.

References