Effect of cation distribution on the properties of Mn$_{0.2}$Zn$_x$Ni$_{0.82}$Fe$_2$O$_4$

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Abstract
Mn$_{0.2}$Zn$_x$Ni$_{0.82}$Fe$_2$O$_4$ ($x = 0.2$, 0.3, 0.4, 0.5, 0.6) are synthesized by the citrate precursor method. Effects of zinc substitution on DC resistivity, dielectric relaxation intensity, initial permeability, saturation magnetization and Curie temperature have been investigated. It is observed that resistivity increases with increase in zinc concentration up to $x = 0.5$ and then decreases. The observed behaviour is explained in terms of hopping and site preference of ions in the lattice. The main contribution to dielectric relaxation intensity is observed to be due to space charge polarization. Initial permeability is observed to increase with increase in zinc concentration. Saturation magnetization increases up to $x = 0.4$ and then starts decreasing. Canting effect is observed for higher zinc concentrations.

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1. Introduction
Mn-Zn ferrites are used for magnetic applications such as transformer cores, noise filters and recording heads, etc. due to their excellent magnetic properties such as high initial permeability and high saturation magnetization. However, these ferrites have certain limitation for magnetic applications at higher frequencies because of their low resistivity and therefore high eddy current losses. Although Ni-Zn ferrites have a wide spread role in many technological applications due to their low eddy currents and dielectric losses, inferior magnetic properties at higher frequencies limit their use. Properties of these ferrites (Mn-Zn and Ni-Zn) have been investigated extensively [1-4], however, very few reports are available on the combination of these two [4,5]. In a previous work, authors have reported [6,7] the electrical and magnetic properties of Mn$_{0.52}$Zn$_{0.48}$Fe$_2$O$_4$ and had observed that optimum properties are observed for $x = 0.2$. In order to aim for further improvement in the properties, Mn$_{0.2}$Zn$_x$Ni$_{0.82}$Fe$_2$O$_4$ have been prepared and investigated for DC resistivity, dielectric relaxation intensity, initial permeability, Curie temperature and saturation magnetization. An attempt has been made to understand the effect of cations distribution on these properties. Several types of wet chemical methods are being used for the improvement of the properties of ferrites. Recently, the citrate precursor method [8] has been proved superior for the preparation of high quality ferrites. Therefore in the present work citrate precursor method has been used for the synthesis of the ferrites.

2. Experimental
In the present work Mn$_{0.2}$Zn$_x$Ni$_{0.82}$Fe$_2$O$_4$ with compositions $x = 0.2$, 0.3, 0.4, 0.5, 0.6 are synthesized by the citrate precursor method. The starting materials—manganese nitrate (98.5%, Merck, Germany), zinc nitrate (96%, Merck, India), nickel nitrate (97%, Merck, India), iron (III) citrate (Merck, Germany) and citric acid (99.5%, Merck, India)—were weighed in stoichiometric proportions. Iron
(III) citrate solution was prepared in distilled water by heating at 40 °C under continuous stirring. Citric acid was added in manganese nitrate, nickel nitrate and iron citrate with a few drops of water. These solutions were heated at 40 °C for 15 min and then added to iron citrate solution. The precursor mixture was evaporated to dryness at 40 °C to obtain a transparent brown colour glossy materials containing the constituent metal ions homogeneously mixed at the atomic level. The powders were calcined at 500 °C for 1 h. X-ray diffraction of all samples were recorded using Rigaku Geiger Flex 3 kW X-ray diffractometer. The binder (polyvinyl alcohol), 2% by weight, was added to the calcined powders. The powders were pressed into pellets (diameter 13.00 mm, thickness 1.25 mm) and toroids (thickness 2.30 mm, inner and outer diameters 7.80 mm and 15.00 mm, respectively) by applying pressures of 10 and 5 Tons, respectively. It has been reported by authors [6,7] in an earlier work that samples sintered at 1200 °C showed better compositional stoichiometry and homogeneity as compared to those sintered at higher temperatures. Therefore, in the present work, all samples were sintered in air for 1 h at 1200 °C. The heating rate was kept at 2.5 °C/min. The SEM photomicrograph of fractured surfaces of all samples was recorded using Cambridge Stereo scan 360 scanning electron microscope. DC resistivity was measured by two-probe method using Keithley electrometer (model 610) of sensitivity $10^{-12}$ A. Dielectric relaxation intensity as a function of frequency in the range from 100 Hz to 13 MHz was calculated from the capacitance measured using a HP 4192A impedance analyzer. Inductance $L$ was measured with a Hewlett Packard impedance analyzer (4192A). Permeability was calculated using the formula $\mu = L/L_0$, where $L_0$ is the air core inductance calculated using the dimensions of the coil. Saturation magnetization was measured with a vibration sample magnetometer of EG and G Princeton Applied Research (model 155). All measurements were carried out at room temperature. The Curie temperature was measured by the arrangement described by Soohoo [9].

3. Results and discussions

The X-ray diffraction patterns of the samples calcined at 500 °C and sintered at 1200 °C show all the expected intense lines of the spinel structure. No additional lines other than spinel structure are seen. Typical diffraction pattern corresponding to the sample $x = 0.6$ is shown in Fig. 1. The values of lattice constant calculated from the observed $d$ values of most intense peaks are shown in Fig. 2. Lattice constant is observed to increase with increase in zinc concentration. Since the ionic radius of $\text{Zn}^{2+}$ (0.82 Å) is greater than that of $\text{Ni}^{2+}$ (0.78 Å), increase in lattice parameter is expected with increase in zinc concentration.

The observed variation of DC resistivity is shown in Fig. 2. With increase in zinc concentration an increase in resistivity followed by a decrease is seen. The observed values, in the range of $10^6$-$10^8$ V cm, are close to those reported by the authors in an earlier work [6]. It is known [10,11] that zinc and nickel ions occupy tetrahedral (A-sites) and octahedral (B-sites) positions, respectively, while the iron and the manganese ions occupy both A and B-sites; however, the probability of finding iron and manganese ions at B and A-sites, respectively, is more. Although, manganese, nickel and iron ions are known to exist in both 2 $\text{+}$ and 3 $\text{+}$ states, manganese and nickel are primarily in the 2 $\text{+}$ while iron is primarily in 3 $\text{+}$ states. The conduction in ferrites is mainly due to hopping of electrons between ions of the same element but of different valence state present at equivalent sites. Production of ions in more than one valence state depends on the preparation conditions such as the sintering temperature [12]. The probability $P$ of electron hopping is given by

$$P \propto \frac{1}{e} \left( \frac{e}{kT} \right) \exp(\frac{-2}{g}) \right),$$

where $r$ is the hopping distance, $j$ is the localization length, $e$ is associated energy, $D(e)$ is the density of energy levels...
Fig. 4. Compositional variation of saturation magnetization and Curie temperature of Mn₀.₂ZnₓNi₀.₈₋ₓFe₂O₄.

associated with the hopping and \( k_B \) is the Boltzmann constant. It is known that distance between metal ions at A-site and B-site is more than that between the two metals ion at B-site. Therefore, B-B hopping probability is more than that of the A-B hopping. The hopping between A-A sites does not exist because iron at A-site exists only in Fe³⁺ state. The compositional variation of resistivity may be due to the following processes:

(a) Increase in zinc concentration decreases some of the already scarce Ni³⁺ concentration at B-site. This reduces the hopping between Ni³⁺ and Ni³⁺ ions at B-site and the resistivity increases.

(b) The Fe³⁺ reduces to Fe²⁺ by the reaction \( \text{Ni}^{2+} + 2 \text{Fe}^{3+} \rightarrow \text{Ni}^{3+} + 2 \text{Fe}^{2+} \). The decrease in Ni³⁺ concentration results in the shift in equilibrium towards backward direction and thereby decreases the Fe²⁺ and Ni³⁺ concentration. This reduces the hopping between Fe³⁺ and Fe²⁺ and between Ni³⁺ and Ni³⁺ at B-site resulting thereby in increase in resistivity with increase in zinc concentration.

(c) When the Zn²⁺ is introduced at the cost of Ni³⁺, some of the Fe³⁺ migrate from A to the B-sites; this is in accordance with the site preference of ions as stated earlier. Since the ionic radius of Fe³⁺ (0.67 Å) is less than that of Ni³⁺, the bond length between metal ions at B-site increases and this reduces the overlapping of orbitals and hence the electron hopping. Therefore, the resistivity is expected to increase with increase in zinc concentration. As a result of the above three processes, resistivity increases with increase in zinc concentration. The decrease in resistivity observed for higher zinc concentration may be due to

(d) Zinc loss due to volatilization is expected at higher sintering temperatures [13]. Since the vapour pressure and melting point of zinc is much lower than those of other elements, probability of zinc evaporation is maximum. It is known [14] that zinc loss results in increase in Fe³⁺ concentration. Therefore for higher zinc concentration the hopping between Fe³⁺ and Fe³⁺ ions increases due to an increase in Fe³⁺ concentration.

(e) For higher zinc concentration, the increased number of Fe³⁺ ions at B-site is expected to enhance \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \) conversion by the process \( \text{Mn}^{3+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{Mn}^{2+} \). The hopping between Fe³⁺ and Fe²⁺ and between Mn³⁺ and Mn³⁺ at B-sites therefore increases.

Processes (d) and (e) contribute to decrease in resistivity at higher zinc concentration and are dominant over processes (a)-(c).

From the measurements of dielectric constant, dielectric relaxation intensity [15], which is the difference between the values of the dielectric constant at low and high frequencies, is calculated. The low and high frequencies for this purpose are taken as 200 Hz and 10 MHz, respectively. The observed variation in the values of dielectric relaxation intensity as a function of composition is shown in Fig. 3. A sharp decrease in dielectric relaxation intensity is observed for lower zinc concentration while for higher zinc concentration slight increase is observed. The dielectric constant at low frequency (200 Hz) is observed to be high (150-650 depending on the \( x \) value) while at high frequency (10 MHz) it is almost constant (15). The variation in dielectric relaxation intensity with composition is therefore primarily governed by changes in interfacial polarization at low frequencies. It can be explained on the basis of electron hopping conduction between Fe³⁺ and Fe²⁺, between Mn³⁺ and Mn³⁺ and between Ni³⁺ and Ni³⁺ pairs of ions. It is well known that ferrite samples consist of conducting grains separated by poorly conducting grain boundaries [16]. The electrons reach the grain boundary through hopping and if the resistance of grain boundary is high enough, electrons pile up at the grain boundaries and produce polarization. This is in accordance with the Maxwell [17] Wagner model [18,19] for space charge polarization due to inhomogeneous
dielectric structure. The space charge polarization is governed by the number of space charge carriers and the resistivity of the sample. As mentioned in the preceding paragraph, resistivity due to processes (a)-(c) increases with increase in zinc concentration. The polarization and hence the dielectric relaxation intensity is therefore expected to decrease. A slight increase in dielectric relaxation intensity for higher zinc concentration is due to increase in space charge polarization as a result of increased electron hopping because of the processes (d) and (e).

It is observed that saturation magnetization increases with increase in zinc concentration up to \( x = 0.4 \) and decreases at higher zinc concentrations, Fig. 4. The observed variation in saturation magnetization can be explained in the terms of exchange interactions between B and A-sites, respectively. The A-B interaction is known to be the strongest and dominates the B-B and A-A interactions. When Fe\(^{3+}\) ion concentration in the A-sublattice is diluted due to the substitution by Zn\(^{2+}\) ion, the site preferences of different ions as mentioned above, the net magnetization, which is the difference between magnetization of B and A-sublattices, increases. At higher substitution levels, there being a very few iron ions left at the A-sites, the A-B interaction as felt by the B-sites iron ions is weakened. Consequently, all the B-site iron spins are no longer held antiparallel to the few remaining Fe\(^{3+}\) spins at A-sites. Thus there is a departure from collinearity of spins of B-site iron ions resulting in canting. The canting effect in mixed Zn ferrites [20,21] has been reported by several workers for higher zinc contents. The net magnetization of lattice, therefore, decreases.

The observed variation of Curie temperature with composition is shown in Fig. 4. The decrease in Curie temperature with increase in zinc concentration is due to the reasons given in the latter part of the preceding paragraph. The increased iron ions at B-sites results in a decrease in A-B interaction as felt by the B-site iron ions without significantly effecting the A-B interaction as felt by the A-site iron ions. The Curie temperature therefore decreases.

Initial permeability is observed to increase with increase in zinc concentration, Fig. 3. Initial permeability increases with increase in grain size and stoichiometry and decreases with increase in porosity and magneto-crystalline anisotropy. Both the grain size and the stoichiometry are reported to increase with increase in zinc concentration in Ni-Zn ferrites [22,23]. The average grain size measured by the linear-intercept method [24] corresponding to samples \( x = 0.2, 0.3, 0.4, 0.5 \) and 0.6 are 0.9, 1.1, 1.5, 1.7 and 2.2 mm, respectively. Typical photomicrograph corresponding to the sample \( x = 0.4 \) is shown in Fig. 5. Because of grain size and stoichiometry variations, the initial permeability is expected to increase with increase in zinc concentration. It is known [25] that magneto-crystalline anisotropy due to Fe\(^{3+}\) is more than that due to Fe\(^{2+}\) ions. The decrease in Fe\(^{3+}\) concentration up to \( x = 0.5 \) and subsequent increase is already explained on the basis of the processes (a)-(e) mentioned earlier. Initial permeability on account of this is therefore expected to increase up to \( x = 0.5 \) and decrease at higher \( x \) values. The increases in porosity which are expected because of increase in lattice parameter, would decrease the initial permeability. The increase in permeability with increase in zinc content as observed in the present work therefore suggests the dominance of the effects of grain size, stoichiometry and magneto-crystalline anisotropy. Above \( x = 0.5 \) the decrease in initial permeability due to increase in the magneto-crystalline anisotropy does not alter significantly the variation in initial permeability.

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References