Magnetic properties of In$^{3+}$ and Cr$^{3+}$ substituted Mg-Mn ferrites

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Abstract

Two series of magnesium-manganese ferrites, viz., Mgo.9Mn$_{0.1}$In$_x$Fe$_{2-x}$O$_4$ and Mgo.9Mn$_{0.1}$Cr$_x$Fe$_{2-x}$O$_4$ have been prepared using conventional ceramic technique. Magnetic properties such as saturation magnetization ($M_s$), Curie temperature ($T_c$), initial permeability ($\mu_i$), and magnetic loss factor ($\tan \delta$), of the above series of samples are presented in this paper. $M_s$ value increases slightly up to a certain concentration of indium ions thereafter it decreases, while in the case of Cr-samples saturation magnetization decreases steadily. The Curie temperature is observed to fall with increasing concentrations of both indium and chromium. The observed variations in $T_c$ and $M_s$ values are explained on the basis of exchange interactions. It is found that compared with Cr$^{3+}$ ions, In$^{3+}$ ions play more significant role in enhancing the initial permeability. The magnetic loss factor values lie in the range of 0.15-0.75 within the frequency range of 10kHz-10MHz. Explanation for the observed variation in $\mu_i$ and $\tan \delta$ with the increasing concentrations of indium and chromium are given.

Keywords: Mg-Mn ferrites; Saturation magnetization; Curie temperature; Initial permeability; Magnetic loss factor; Exchange interactions

1. Introduction

Magnesium-manganese ferrites are widely used in switching devices due to their spontaneous rectangular-hysteresis-loop behavior with high rectangularity ratio [1-3]. Low permeability, low saturation magnetization, very high resistivity and low Eddy current losses even at microwave frequencies are some of the characteristic properties of Mg-Mn ferrites. These properties mainly depend on the amounts of ingredients present and the method of preparation. The selection of a ferrite material for specific application mainly depends on the basic constituents of the composition.

The basic composition Mg0.9Mn0.1Fe$_2$O$_4$ has been doped with trivalent indium and chromium ions to study their effect on the magnetic properties such as saturation magnetization, Curie temperature, initial permeability and magnetic loss factor.
2. Experimental

The following two series of magnesium-manganese ferrites have been prepared from basic composition $Mg_{0.9}Mn_{0.1}Fe_{2}O_{4}$ by gradually replacing $Fe_{2}O_{3}$ with $In_{2}O_{3}$ and $Cr_{2}O_{3}$:

(i) $Mg_{0.9}Mn_{0.1}In_{x}Fe_{2-x}O_4$ (hereafter referred as In-series),
(ii) $Mg_{0.9}Mn_{0.1}Cr_{y}Fe_{2-y}O_4$ (hereafter referred as Cr-series),

where $x$ or $y$ vary from 0.1 to 0.9 in steps 0.2. Highly pure analytical reagent grade $MgO$ (98%), $MnO$ (99.9%), $Fe_2O_3$ (99.9%), $In_2O_3$ (99.97%) and $Cr_2O_3$ (99.8%) were used for the preparation of the ferrites by conventional ceramic technique. The proper amounts of ingredients were crushed and mixed thoroughly for 5 h in acetone using an agate mortar and pestle in an electrical grinder. The mixture was dried and calcined at 950°C for 4 h followed by furnace cooling in air atmosphere. The presintered material was again crushed and mixed for another 5 h in acetone to reduce it to small crystallites of uniform size. The mixture was dried and a few drops of saturated solution of polyvinyl alcohol were added as a binder. The material was granulated through sieves of 60–80 mesh BSS (250-180 mm approx.) and the granules were compressed uniaxially under a pressure of 8 tons/in$^2$ in stainless-steel dies to make pellets of about 13 mm diameter and toroids of 9 mm inner diameter and 15 mm outer diameter. The pellets and toroids were then finally sintered at 1350°C for 4 hrs in air followed by furnace cooling. The surfaces of all the samples were ground to remove any oxide layer formed during sintering.

The X-ray diffraction analyses confirmed the single-phase cubic spinel structure for all the samples. Saturation magnetic moment was measured using a vibrating sample magnetometer (EG&G PARC Model 155). A simple experimental setup described by Soohoo [4] was used to measure the Curie temperature. Initial permeability of toroidal samples was determined following the method described by Heck [5]. About 20 turns of 30 SWG enameled copper wire were wound on these toroids and the inductance, $L$, was measured at various frequencies (ranging from 10 Hz to 10 MHz) using a Hewlett Packard LCR Meter Bridge Model 4275 A. The initial permeability was calculated using the relation

$$\mu_i = \frac{L}{L_0},$$

where

$$L_0 = 4.6 N^2d \log \frac{OD}{ID} \times 10^{-7} \text{ H}.$$ 

$L_0$ is the air-core inductance, $N$ is the number of turns and $d$ is the thickness of the toroid. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Saturation magnetization

The observed variations of saturation magnetization with concentrations of indium and chromium ions in $Mg_{0.9}Mn_{0.1}In_{x}Fe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Cr_{y}Fe_{2-y}O_4$ are shown in Fig 1. An incorporation of 5mol% ($x = 0.1$) indium ions

![Graph showing variation of saturation magnetization with composition.](image)
increases saturation magnetization value of the basic composition by about 10% and the rise in saturation magnetization continues further to attain a peak value in the range of 0.1 to 0.3. For higher concentrations of indium, the saturation magnetization decreases rapidly and a fall of about 79% was recorded in the concentration range from \( x = 0.3 \) to 0.7. In the case of Cr series, the initial decrease in saturation magnetization is less for \( y = 0.1 \) followed by a steady fall with increasing concentrations of chromium. The fall of about 73% was recorded in the concentration range from \( y = 0.1 \) to 0.9.

Neel [6] considered three kinds of exchange interactions between unpaired electrons of two ions lying: (i) both ions at A-sites (AA interaction), (ii) both ions at B-sites (BB interaction), and (iii) one at A-site and the other at B-site (AB interaction). AB interaction heavily predominates over AA and BB interactions. The AB interaction aligns all the magnetic spins at A-site in one direction and those at B-site in the opposite direction. The net magnetic moment of the lattice is therefore the difference between the magnetic moments of B and A sublattices, i.e., \( M = M_B - M_A \). To explain the observed variation in saturation magnetization, the following possibilities may be considered:

(i) In\(^{3+}\) ions occupy B-sites and replace Fe\(^{3+}\) ions.
(ii) In\(^{3+}\) ions replace A-site Fe\(^{3+}\) ions,
(iii) In\(^{3+}\) ions occupy A-sites and push Mn\(^{2+}\) ions from A- to B-sites.
(iv) In\(^{3+}\) ions occupy both A- and B-sites.

If indium ions occupy B-sites and replace B site Fe\(^{3+}\) ions, the magnetization of B-sublattice decreases keeping the magnetization of A-sublattice constant. Thus, the resultant magnetization according to \( M = MB + MA \) is expected to decrease which is contrary to the observed rise in saturation magnetization for \( x = 0.1 \). Therefore, possibility (i) is ruled out. For lower concentrations, if In\(^{3+}\) ions occupy A-sites and replace Fe\(^{3+}\) ions, A-sublattice magnetization decreases and the resultant magnetization, therefore increases. From the Mossbauer spectra the peak intensity corresponding to A-site Fe\(^{3+}\) ions is observed to be constant for \( x \) value around 0.1 which indicates that In\(^{3+}\) ions occupy A-sites and push the Mn\(^{2+}\) from A- to B-sites [7]. Because of this, the magnetization of A-sub lattice decreases keeping B-sub lattice magnetization almost constant. Moreover, in the basic composition, as manganese content is only 5 mol%, indium ions could have pushed all the Mn\(^{2+}\) ions to B-sites for \( x = 0.1 \). With further increase in \( x \), In\(^{3+}\) ions start replacing Fe\(^{3+}\) ions from A-sites and thereby magnetization of A-sublattice decreases further. This process explains the observed increase in saturation magnetization up to \( x \geq 0.3 \). The possibilities (ii) and (iii) are therefore possible. A similar explanation was offered by others in understanding the observed increase in magnetization with the introduction of small amounts In\(^{3+}\) ions in Mn-Zn ferrites [8,9].

For higher concentrations, \( x > 0.3 \); if indium ions continue to occupy A-sites, the magnetization of A-sublattice would decrease rapidly which in turn weakens AB-exchange interactions considerably and the material may turn into paramagnetic. But the moderate values in saturation magnetization and Curie temperature for samples with \( x > 0.3 \) indicate that the AB exchange interaction still persists for these samples. This shows that at higher concentration, indium may partly occupy B-sites and replace Fe\(^{3+}\) ions due to which AB exchange interactions, though weakens, is strong enough to provide some magnetization.

The experimental values of Curie temperature, Fig 2, even for \( x \) up to 0.7 indicates that AB exchange interactions are effective in samples with high indium content. It may thus be concluded that indium ions occupy A-sites for \( x \leq 0.3 \) and for higher concentrations the indium ions may occupy B-sites also. Similar observations were made by others too [10,11].

The saturation magnetization for \( x = 0.9 \) sample could not be obtained due to its paramagnetic state which is further supported by Curie temperature measurements.

The saturation magnetization is observed to decrease with increasing paramagnetic chromium content throughout the concentration range studied. It is well known that Cr\(^{3+}\) ions preferably
occupy B-sites [12]. As the number of Fe\(^{3+}\) ions at B-site continuously decreases, the magnetization of B-sub lattice decreases which results into the observed decrease in saturation magnetization for Cr-series. A similar decrease was reported in Mn-Zn-Cr ferrites [9] and also in non-stoichiometric Mg-Mn-Cr ferrites [13]. Unlike indium substituted samples, chromium samples have exhibited saturation magnetization up to the maximum concentration of y = 0.9. This indicates that the exchange interactions persist in all the samples of Cr-series, which is further supported by the Curie temperature values. At higher concentrations the fall in saturation magnetization for In-series is observed to be more than that of Cr-series. As seen earlier, with the introduction of higher concentration of indium, the number of Fe\(^{3+}\) ions from both A- and B-sites get diluted simultaneously, while in the case of chromium substitution, only the number of B-site iron ions decreases. Thus, AB exchange interactions in the case of In-series weaken more rapidly and thereby the saturation magnetization decreases faster.

3.2. Curie temperature

The observed fall in Curie temperature with increasing concentrations of indium and chromium is shown in Fig 2. The variation is observed to be more rapid in indium substituted samples. For any given concentration, Curie temperature value for chromium substituted samples is higher than that of indium samples.

It is well known that the replacement of Fe\(^{3+}\) ions by the paramagnetic or diamagnetic ions results in the fall of Curie temperature [8-10,14,15]. The observed variations in Curie temperature for both the series may be explained on the basis of exchange interactions. As the exchange interactions between the magnetic ions in A- and B-sublattices increase with both the density and the magnetic moment of the magnetic ions, greater amount of thermal energy is required to off set the effects of exchange interactions.

When Fe\(^{3+}\) ions are replaced by diamagnetic In\(^{3+}\) ions, the magnetic moment of A-sublattices will be reduced and net magnetic moment decreases. Consequently, the Curie temperature decreases with increasing indium ions in Mg-Mn ferrites. For a sample with indium content x = 0.9, the Curie temperature measurements could not be carried out as it turned out to be paramagnetic at room temperature, and thus its Curie temperature value lies below room temperature.

When Fe\(^{3+}\) ions at B-site are replaced by paramagnetic Cr\(^{3+}\) ions, B-sublattice magnetization decreases without affecting the A-sublattice magnetization, which in turn weakens AB exchange interaction. As paramagnetic chromium ions weakly participate in exchange interactions, AB exchange interaction is expected to exist throughout the concentration studied. The observed fall in Curie temperature in the Cr-series is attributed to partial weakening of AB exchange interactions.

3.3. Initial permeability

The room temperature initial permeability, \(m_i\), was measured at low field of 0.47 G and at applied frequency of 10 kHz for all the samples. The \(m_i\) values are corrected to the theoretical density against the increased contents of In\(_2\)O\(_3\) and Cr\(_2\)O\(_3\), so as to eliminate the effects of the pores present between the grains on the values of \(m_i\). The
corrected initial permeability is denoted by \( (\mu_r - 1) \). Fig. 3 shows the variations of corrected initial permeability with increasing concentrations of In and Cr ions. The initial permeability for \( x = 0.7 \) and \( y = 0.9 \) were too low to be measured. A remarkable increase in the initial permeability is witnessed with increasing concentration of indium and its maximum value is achieved for \( x = 0.5 \). An insignificant raise in initial permeability has been observed for \( \text{Cr}^{3+} \) substituted samples. A similar increase in initial permeability was reported earlier with the addition of diamagnetic \( \text{Al}^{3+} \) in a typical \( \text{Mg-Mn} \) ferrite [14]. In the recent work of Singh and Sud [15] the increase in initial permeability was reported with the doping of indium ions in \( \text{Mg-Mn} \) ferrites.

The observed variations in initial permeability may be explained by the following considerations. The initial permeability of a ferromagnetic material depends on many factors like reversible displacement of domain walls, bulging of domain walls as well as microstructural parameters viz., average grain size, intra-granular porosity, etc. [16]. Perduijn and Peloschek [17] and Roess et al. [18] found a linear relation between the initial permeability and grain size in \( \text{Mn-Zn} \) ferrites. Globus and co-workers [19] investigated several \( \text{Ni-Zn} \) ferrites and also found a linear relationship.

Deviations from linearity have also been reported in some cases [20].

As the observed grain size variation is insignificant [7] the considerable rise in initial permeability with increasing concentrations of indium cannot be mainly attributed to the grain size values. Besides, the scanning electron micrographs [7] revealed the presence of pores, which will hinder the motion of domain walls and decrease initial permeability. The observed large increase in initial permeability is therefore in contradiction. Thus, some mechanisms other than the microstructural properties play the key role in the observed variation of initial permeability in the In-series. It is also known [16] that initial permeability of a ferrite is directly proportional to the square of the saturation magnetization and inversely proportional to the crystalline anisotropy constant. The observed increase in the initial permeability could be due to combined effect of these two phenomena. An insignificant increase in the corrected initial permeability is observed with increasing concentrations of chromium. In spite of the fall in saturation magnetization as well as in the density in \( \text{Cr-series} \), the insignificant rise in \( \mu_i \) is not well understood. The scanning electron micrographs for these \( \text{Cr-substituted} \) samples reveal pore-free grains with unsystematic variation in grain size values [7]. The microstructural modifications do not, therefore, play major role in the observed slight rise in \( \mu_i \).

3.4. Magnetic loss factor

The magnetic loss factor values, or simply \( \tan \delta \), measured at room temperature lie within the range of 0.15-0.75 for the given frequency limits 10 kHz to 10 MHz for both the series. These values are fairly low. Fig. 4 shows the compositional dependence of magnetic loss factors at 10 kHz and 10 MHz for both the series. At 10 kHz, the loss factor decreases with increasing indium ions, while it remains unchanged for chromium concentration up to 25 mol% beyond which the loss factor decreases. At higher frequency of 10 MHz, loss factor is observed to increase with increasing concentrations of indium as well as chromium. It is noted that for In-series, the loss factor values are
higher compared to that for Cr-series, which may be due to the higher values of initial permeability for indium substituted samples.

The major contribution to the magnetic losses in ferrites is due to hysteresis losses, which in turn is based on damping phenomena associated with irreversible wall displacement and spin rotations. However, the hysteresis loss becomes less important in the high-frequency range because the wall displacement is mainly damped and the hysteresis loss will be due to spin rotation.

The frequency range used in the present study was too low to obtain a complete dispersion pattern regarding the frequency dependence of initial permeability and magnetic loss factor.

4. Conclusions

The $M_s$ values initially increase with the addition of In$^{3+}$ ions and show a rapid decrease at higher concentrations. In the case of Cr$^{3+}$ addition, the $M_s$ value steadily decreases with increasing concentration of the ions. Curie temperature has been found to decrease with the successive addition of In$^{3+}$ and Cr$^{3+}$ ions. A remarkable increase in the value of initial permeability has been found with increasing indium up to $x = 0.5$. An insignificant rise in the initial permeability was observed for the Cr-series. Magnetic loss tangent values are very low in the frequency range 10 kHz to 10 MHz.

References