Improvement of the magnetic properties for Mn–Ni–Zn ferrites by rare earth Nd\textsuperscript{3+} ion substitution

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\textbf{ABSTRACT}

Single spinel phases of Mn\textsubscript{0.5}Ni\textsubscript{0.1}Zn\textsubscript{0.4}Nd\textsubscript{x}Fe\textsubscript{2−x}O\textsubscript{4} ferrite samples (x = 0.0, 0.01, 0.02, 0.05, 0.075, and 0.1) have been prepared by ceramic method and the composition dependence of the physical and magnetic properties has been investigated. SEM micrographs and EDX analysis revealed that there is no considerable effect for the Nd\textsuperscript{3+} ion substitution on the average grain size or porosity, whereas its concentration in the grain boundaries is higher than that in the grains. Saturation magnetization (M\textsubscript{S}) increased with the Nd\textsuperscript{3+} ion concentration (x) and reached a maximum value at x = 0.05. In addition, both the initial permeability and the magnetic homogeneity increased by increasing the Nd\textsuperscript{3+} ion content. The value of Curie temperature increased due to the substitution by Nd\textsuperscript{3+} ions to record about 170 K, for the sample with x = 0.05, higher than that of the un-substituted one.

Introduction

Both Mn–Zn and Ni–Zn ferrites have a great importance from the application point of view, where they are used in many ferrite devices such as inductor cores, converters, magnetic heads, and electromagnetic wave absorbers. Although Mn–Zn ferrites have distinctive magnetic properties as high initial permeability and magnetization, they have low electrical resistivity and high power losses. So, they are not suitable for magnetic applications especially at high frequencies. On the other hand, Ni–Zn ferrites are characterized by their high resistivity, low dielectric loss and high Curie temperature, but they have relatively low initial permeability at high frequencies. Combinations between these two ferrites were carried out by many studies trying to obtain favorable magnetic properties with low losses especially at high frequencies in bulk and powder forms [1–10]. In a previous work, the magnetic and electrical properties of such a combination were investigated [11,12]. The sample with the chemical formula Mn\textsubscript{0.5}Ni\textsubscript{0.1}Zn\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4} was found to possess the optimum properties for promising applications.
type of substituted ions [2,12]. Accordingly, this work deals with the improvement of the magnetic properties of this last optimum sample when Nd$^{3+}$ ions substitute only Fe$^{3+}$ ions. This may present a candidate for magnetic applications in high frequency field.

Material and methods

Ferrite samples with the chemical formula Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Nd$_x$Fe$_{2-y}$O$_4$ ($x = 0.0$, 0.01, 0.02, 0.05, 0.075 and 0.1) were prepared by the usual standard ceramic method. Details about the preparation conditions were previously reported [11]. X-ray diffraction patterns were performed using a diffractometer of type X’Pert Graphics and identified with Cu K$\alpha$ radiation. The Scanning Electron Microscope (SEM) of type PARC model no. 1551 USA. The porosity percentage ($P$) and the initial permeability ($\mu_i$) were measured according to the ASTM intercept method. This method takes three parameters in consideration: the energy dispersive X-ray spectrometer (EDX) was used to analyze both the grain and the grain boundaries. The magnetization was measured for powder samples, at room temperature, using Vibrating Sample Magnetometer (VSM, EG&G PARC model no. 1551 USA). The porosity percentage ($P$) and the initial permeability ($\mu_i$) were measured according to the techniques and methods mentioned elsewhere [11,12].

Results and discussion

X-ray diffraction

X-ray diffraction patterns, (Fig. 1), showed that all the investigated samples have single cubic spinel phase. Values of the lattice parameter ($a$) were calculated according to the procedure mentioned before [14]. Fig. 1 shows the variation of the lattice parameter as a function of Nd-concentration ($x$). It can be seen that the lattice parameter decreases dramatically with the Nd-concentration up to $x = 0.05$ then it becomes nearly constant for $0.05 < x \leq 0.1$. For $x \leq 0.05$, the decrease in the lattice parameter could be attributed to that some rare earth ions reside at the grain boundaries [15]. Hence, they hinder the grain growth and may exert a pressure on the grains and lead the lattice parameter to decrease. The presence of higher concentrations of Nd$^{3+}$ ions in the grain boundaries than that in the grains was confirmed by EDX analysis and it will be discussed in the next section. On the other side, for $0.05 < x \leq 0.1$, some of the Nd$^{3+}$ ions (radius = 0.983 Å) [16] that substitute Fe$^{3+}$ ions (radius = 0.645 Å) [16] in the unit cell may cause the increase in the lattice parameter which in turn compensates the decrease due to the grain boundaries pressure.

Porosity, SEM and EDX

The composition dependence of porosity is illustrated in Fig. 2. One can note the absence of any considerable change in the value of porosity by increasing the Nd-content. This could be linked to the constancy in the average value of the grain size shown by SEM micrographs.

Fig. 3 shows the SEM micrographs for the samples with $x = 0.0$, 0.05, and 0.1. It is obvious that the substitution by Nd$^{3+}$ ions in our system has no noticeable effect on the grain size. The average value of the grain size determined by ASTM intercept method is about 4.2 μm.

The energy dispersive X-ray spectra (EDX) for the sample with $x = 0.05$ at the grain and grain boundaries are represented in Fig. 4. The analysis of EDX data is collected in two tables as insets in the same figure. Each table contains two columns; one is for the element percentage and the other is for the atomic percentage. The element percentage values represent the raw data of the emitted X-ray intensities which arrive to the detector of the EDX spectrometer. On the other hand, the atomic percentage values come from three iterations for the ZAF quantitative method. This method takes three parameters in consideration: the atomic number of each element ($Z$), the absorption of the emitted X-ray by the sample elements themselves ($A$), and the amount of X-ray fluorescence which results from the sample elements due to the absorption of emitted X-ray ($F$). One can note that the element percentage data show that the concentrations of elements are in non-stoichiometric proportion form,

![Fig. 1 X-ray diffraction patterns for Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Nd$_x$Fe$_{2-y}$O$_4$.](image-url)
whereas the atomic percentage one is nearly fully stoichiometric. The difference between the data of the two columns could be discussed according to the previously reported parameters of the ZAF quantitative method. Although the concentration of O element in the prepared sample is higher than that of Fe, the element percentage value of oxygen is lower than that of iron. This could be attributed to the energy of the emitted oxygen X-ray which is much lower than that of iron. The lower the energy the lower the penetration, so the amount of X-ray arrives to the detector from O anions is lower than that arrives from Fe cations. Moreover, some traces of Cl element were detected in grain boundaries. These traces remained after washing the sample through the etching process.

One of the clearest remarks in these tables is that the concentration of Nd element in the grain boundaries, in both columns, is more than twice that in the grains. In other words, the Nd$^{3+}$ rare earth ions in our ferrite system tend to concentrate in the grain boundaries, which is in agreement with the previously reported results [17,18].

Fig. 3 SEM micrographs for Mn$_{0.3}$Ni$_{0.1}$Zn$_{0.6}$Nd$_{x}$Fe$_{2-x}$O$_4$ ferrite samples with $x = 0.0$, $0.05$, and $0.1$.

Magnetic studies

Magnetization

The variation of the magnetization $M$ (emu/g) versus the applied magnetic field $H$ (Oe), at room temperature, is illustrated in Fig. 5. The dependence of the saturation magnetization ($M_S$) on the Nd-concentration ($x$) is shown in an inset in Fig. 5. It can be seen that $M_S$ increases with $x$ and attains a maximum value at $x = 0.05$ with a percentage increase of 26.5% relative to that of the un-substituted sample. Further increase in the Nd-concentration leads $M_S$ to decrease but with values still larger than that for the sample with $x = 0$. Such a result could be discussed assuming the following cation distribution:

$$ (Zn^{2+}_{0.4}Mn^{2+}_{0.1}Fe^{3+}_{0.5})[[Ni^{2+}_{0.1}Mn^{2+}_{0.1}Nd^{3+}_{x}Fe^{3+}_{2-x}]] $$

where the brackets () and [ ] denote A- and B-sites, respectively. Such a cation distribution is based on the following facts:

1. Zn$^{2+}$ ions have a strong preference to occupy the A-site [19].
2. 80% of Mn$^{2+}$ ions occupy the A-site while 20% occupy the B-site [20].
3. Rare earth ions, as Nd$^{3+}$, occupy the B-site [17,18,21].
According to the assumed cation distribution, the total magnetization \( M_{\text{mol}} = M_B - M_A \), where \( M_A \) and \( M_B \) are the magnetizations of A- and B-sites respectively, is expected to be
\[
M_{\text{mol}} = (6.7 - 1.5x)\mu_B
\]
where \( \mu_B \) is Bohr magneton. It is valuable to note that for Mn–Zn and Ni–Zn ferrites, there exists a canting Yafet-Kittel angle \( (\theta_{\text{YK}}) \) between moments in B-sites at Zn-concentration 0.4. This angle depends on the relative strength of B–B to A–B interactions [11,12,22]. In this case, the last equation could be rewritten as
\[
M_{\text{mol}} = (6.7 \cos \theta_{\text{YK}} - 1.5x)\mu_B
\]

It is suggested that for \( 0 \leq x \leq 0.5 \), substituting Fe\(^{3+}\) ions (moment = 5 \( \mu_B \)) by Nd\(^{3+}\) ions (moment = 3.5 \( \mu_B \)) leads the B-B interaction between these moments to decrease and hence the canting angle \( (\theta_{\text{YK}}) \) decreases. Such a decrease in \( (\theta_{\text{YK}}) \) improves the parallelism between the magnetic moments in the B-site and leads to increase \( M_S \) according to Eq. (2) to reach its maximum value at \( x = 0.05 \). For more substitution by Nd\(^{3+}\) ions \( (x > 0.05) \), the canting angle \( (\theta_{\text{YK}}) \) could be neglected and hence \( M_S \) decreases due to equation (1), where the value of magnetic moments in the B-site decreases and hence the value of \( M_S \) goes down.

**Initial permeability**

Fig. 6 shows the variation of the initial permeability \( \mu_i \) with temperature for the investigated system. It is seen that the initial permeability decreases with temperature up to Curie temperature \( T_C \). There is a sharp drop in \( \mu_i \) near \( T_C \). This result could be explained according to Globus relation [23] which is given by
\[
\mu_i \propto \left( M_S^2 D / k_1 \right) \frac{1}{2}
\]
where \( D \) is the average grain size and \( k_1 \) is the anisotropy constant. It was reported that for Mn–Zn ferrites, the anisotropy constant is independent of temperature for temperatures higher than the room temperature [24]. Accordingly, the decrease in \( \mu_i \) with temperature can be attributed to the decrease in saturation magnetization. At \( T_C \), \( M_S \) drops sharply with temperature leading to the rapid decrease in \( \mu_i \). Moreover, one can notice from Fig. 6 that the slope of the linear part of \( \mu(T) \) curve, at the sudden decrease in \( \mu_i \), increases with increasing Nd\(^{3+}\) concentration. Previous studies have reported that the value of \( (|d\mu / dT|)_{T=T_C} \) gives a good indication about the sample homogeneity where higher slope corresponds to higher homogeneity [23,25]. Thus, one can conclude that the homogeneity increases with increasing Nd-concentration.

The dependence of the initial permeability \( \mu_i \) at room temperature, on Nd\(^{3+}\) ion concentration is represented in Fig. 7. It is clear that \( \mu_i \) increases with increasing Nd-concentration. To explain this behavior, the following aspects have to be taken in consideration. The SEM micrographs revealed that the average grain size \( D \) is nearly independent of the Nd-concentration \( (x) \). Moreover, the increase in \( x \) leads to a decrease in the iron ions concentration in the ferrite molecule. It is well known that the main source of anisotropy in ferrites is the presence of Fe\(^{3+}\) ions [22]. Hence, the anisotropy constant \( k_1 \) decreases. This decrease in the value of \( k_1 \) in turn increases \( \mu_i \) according to Globus relation. Furthermore, the enhancement of \( M_S \) due to the Nd\(^{3+}\) ion substitution enforces the increase in \( \mu_i \) for the samples with \( 0 \leq x \leq 0.05 \).
Values of Curie temperature \( (T_C) \) were determined from the extrapolation of the linear part at the sudden decrease in \( \mu_i \) with temperature, Fig. 6, for all investigated samples. The dependence of \( T_C \) on Nd\(^{3+} \) ion concentration is shown in Fig. 7. It is clear that \( T_C \) increases considerably with increasing Nd-content (about 170 K for the sample with \( x = 0.05 \) higher than that with \( x = 0 \)). For \( x > 0.05 \), \( T_C \) decreases but its value is still higher than that of the un-substituted sample. One can notice from Figs. 5 and 7 that generally \( M_S \) and \( T_C \) behave in a same manner. The increase in \( T_C \) for \( 0 \leq x \leq 0.05 \) with Nd-content could be understood in view of the behavior of both \( M_S \) and the lattice parameter (a). The decrease in (a), Fig. 2, and the increase in \( M_S \), Fig. 5, with increase in the Nd-content lead to increase the A–B interaction between the moments. This in turn increases the value of \( T_C \). On the other hand, for \( x \geq 0.05 \), the constancy in the value of (a), Fig. 2, and the decrease in \( M_S \), Fig. 5, lead the A–B interaction between moments to decrease and, hence, \( T_C \) goes down.

Conclusions

– Single phase Mn\(_{0.3}\)Ni\(_{0.1}\)Zn\(_{0.6}\)Nd\(_{0.1}\)Fe\(_{2}\)O\(_4\) ferrite samples up to \( x = 0.1 \) were obtained.
– Nd\(^{3+} \) ions were found to concentrate in grain boundaries more than in grains, and they had no effect on both average grain size and porosity.
– The saturation magnetization increased by Nd\(^{3+} \) substitution up to 26% relative to that of the un-substituted sample.
– Both initial permeability and Curie temperature were increased due to the Nd\(^{3+} \) substitution from (111 to 442) and from (448 K to 627 K), respectively.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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