

Synthesis, microstructure and magnetic properties of Ni-Mg ferrites

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The effect of compositional variation on the structure and magnetic properties of Ni-Mg ferrites with compositions $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ for $[x = 0.0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0]$, prepared by a conventional double sintering ceramic technique, sintered at 1350°C for 4.5 hours were investigated. The structural characterization of the samples has been performed by X-ray diffraction (XRD). X-ray diffraction results confirmed the single-phase spinel structures of all the ferrite samples. The lattice parameters have been found to increase linearly with increasing Mg concentration, obeying Vegard's law. The bulk density and X-ray density of the samples decrease monotonically with increasing Mg content. SEM micrographs exhibit a decrease in grain size with increasing Mg content. The Curie temperature of Ni-Mg ferrites was found to decrease with an increase in the Mg^{2+} content due to the reduction of A-B exchange interactions. The complex initial permeability is found to decrease as the Mg content increases which is consistent with the variation of density with Mg ions.

Key words: XRD, Lattice parameter, Microstructure, Permeability, Curie temperature.

Introduction

Properties of spinel ferrites are known to be sensitive to the processing technique. A small deviation in the compositional stoichiometry of a ferrite affects its property greatly. Ferrites are commonly produced by a ceramic process involving high temperature solid-state reactions between the constituent oxides [1, 2]. Due to the remarkable magnetic and electric properties, they are subjects of intense theoretical and experimental investigations for application purposes. These polycrystalline spinel ferrites are widely used in many electronic devices. They are preferred because of their high permeability and saturation magnetization in the radio-frequency (RF) region, high electrical resistivity, mechanical hardness and chemical stability. In the spinel structure AB_2O_4 , the anions (O^{2-} ions) form cubic close packing, in which the interstices are occupied by tetrahedral (A-sites) and octahedral (B-sites) coordinated cations. In such magnetic oxide materials the competition between ferromagnetic and antiferromagnetic superexchange interactions occurs between the relative strength of the exchange constants J_{AB} , J_{AA} and J_{BB} . In general, J_{AB} is stronger than both of J_{AA} and J_{BB} . Substitution of nonmagnetic ions on a sublattice leads to the large effect in controlling structural, electrical and magnetic properties [3].

Mg-based ferrite is a pertinent magnetic material due to its high resistivity, relatively high Curie temperature,

low cost, high mechanical hardness and environmental stability. The structural and magnetic properties of ferrites are effectively changed by Mg substitution. Several investigations of the Mg-substituted ferrites have been reported in the literature [4-6]. However no study has been found in the literature correlating the microstructure and the effect of grain size with the magnetic properties of Ni-Mg ferrites. Therefore, in the present research the influence of Mg substitution on the structural and magnetic properties of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ferrites has been investigated.

Experimental

NiO, MgO and Fe_2O_3 of high purity were mixed homogeneously with the appropriate ratios of cations and wet milled in a steel ball mill for 6 h. The samples were dried and the dried powder was pressed into disk shapes. The disk shaped samples were pre-sintered at 800°C for 3 h in air to form ferrites through a solid-state reaction. The raw ferrite was wet milled extensively to get fine powder. The powder was then dried and mixed with polyvinyl alcohol as a binder for granulation. Then the granular powder was pressed into the desired shape using metal dies. The pressed products were sintered at 1350°C in air for 4.5 h. Formation of a ferrite was confirmed by Philips analytical X-ray diffractometer (XRD) using CuK_α radiation. The crystal structure was determined from the XRD data. The microstructures images were taken by a scanning electron microscope (SEM). Curie temperature measurements were performed using an impedance analyzer with a laboratory-built oven and a thermocouple-based thermometer.

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Results and Discussions

XRD analysis

The phase identification and lattice parameter determination were performed on an X-ray diffraction patterns. Typical XRD pattern of the samples of the system $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ are shown in Fig. 1. All the samples show good crystallization, with well-defined diffraction lines. The XRD patterns for all samples clearly show their spinel phase and the formation of a spinel structure. The peaks (220), (311), (222), (400), (511) and (440) correspond to the spinel phase. Our results are confirmed by comparing with the reported values [7].

The lattice parameter was determined through the Nelson-Riley extrapolation method. The values of the lattice parameter obtained from each reflected planes are plotted against the Nelson-Riley function [8]:

$$F(\theta) = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \quad (1)$$

where θ is the Bragg's angle and straight lines are obtained. The accurate values of the lattice parameter were estimated from the extrapolation of these lines to $F(\theta) = 0$ or $F(\theta) = 90^\circ$. The variation of lattice parameter

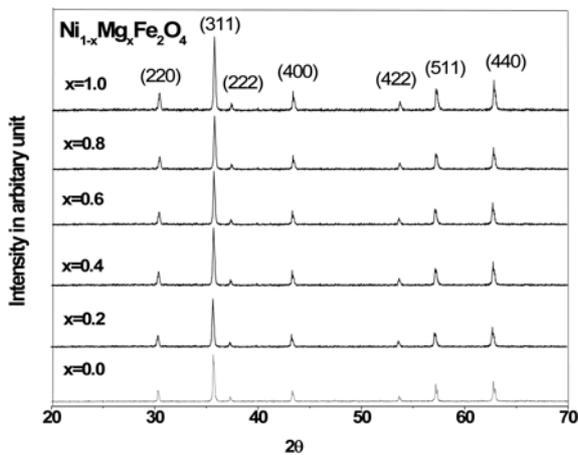


Fig. 1. XRD patterns of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ferrites

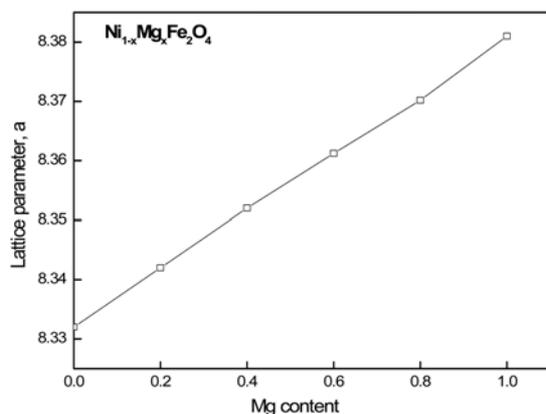


Fig. 2. Variation of the lattice parameter with Mg content in $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$.

as a function of Mg^{2+} content is depicted in Fig. 2. It is noticed that the lattice parameter increases with the Mg content, obeying Vegard's law [9]. This variation can be explained on the basis of an ionic size difference of the component ions. The Mg^{2+} (0.86 Å) ions have a larger ionic radius than Ni^{2+} (0.83 Å) and Fe^{3+} ions (0.64 Å) [10]. A small amount of magnesium occupies the tetrahedral A-sites. Hence the increase in lattice parameter is attributed to the replacement of smaller Fe^{3+} ions from A-sites to B-sites by larger Mg^{2+} . The Mg^{2+} ions successfully replace the Fe^{3+} ions in B-sites. The unit cell expands to accumulate the larger ions. Thus the addition of Mg^{2+} ion is expected to increase the lattice parameter.

The bulk density (ρ_B) was measured by the usual mass and dimensional considerations whereas the X-ray density (ρ_X) of the prepared samples was calculated using the relation:

$$\rho_X = \frac{ZM}{Na^3} \quad (2)$$

where M is the molecular weight of the corresponding composition. N is Avogadro's number, $V = a^3$ is the volume of the cubic unit cell and Z is the number of molecules per unit cell, which is 8 for the spinel structure. The X-ray density is expected to decrease with the Mg content because the lattice parameter increases with Mg content. Similar result has been observed by Pandit *et al.* in Mg-Mn ferrites [11]. The bulk density is lower than the X-ray density. This may be due to the existence of pores which were formed and developed during the sample preparation or the sintering process. Fig. 3 shows the variation of bulk density and X-ray density of the samples. It is observed that the density of the samples decreases linearly with the Mg content. The decrease in densities can be ascribed to the atomic weight and density of Mg^{2+} (24.31 and 1.74 gm/cm^3 , respectively), which are lower than those of Ni^{2+} (58.69 and 8.90 gm/cm^3) and Fe^{3+} (55.85 and 7.86 gm/cm^3) [12].

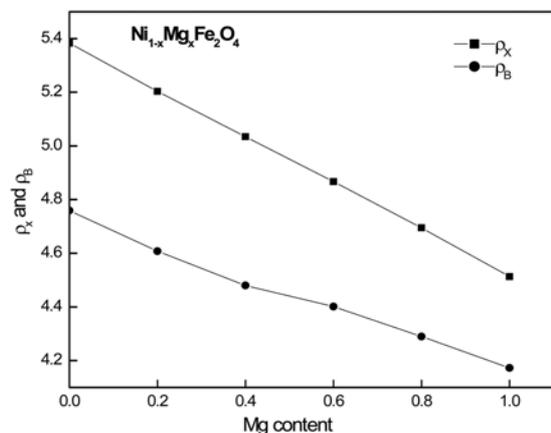


Fig. 3. Variation of the X-ray density and bulk density with Mg content in $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$.

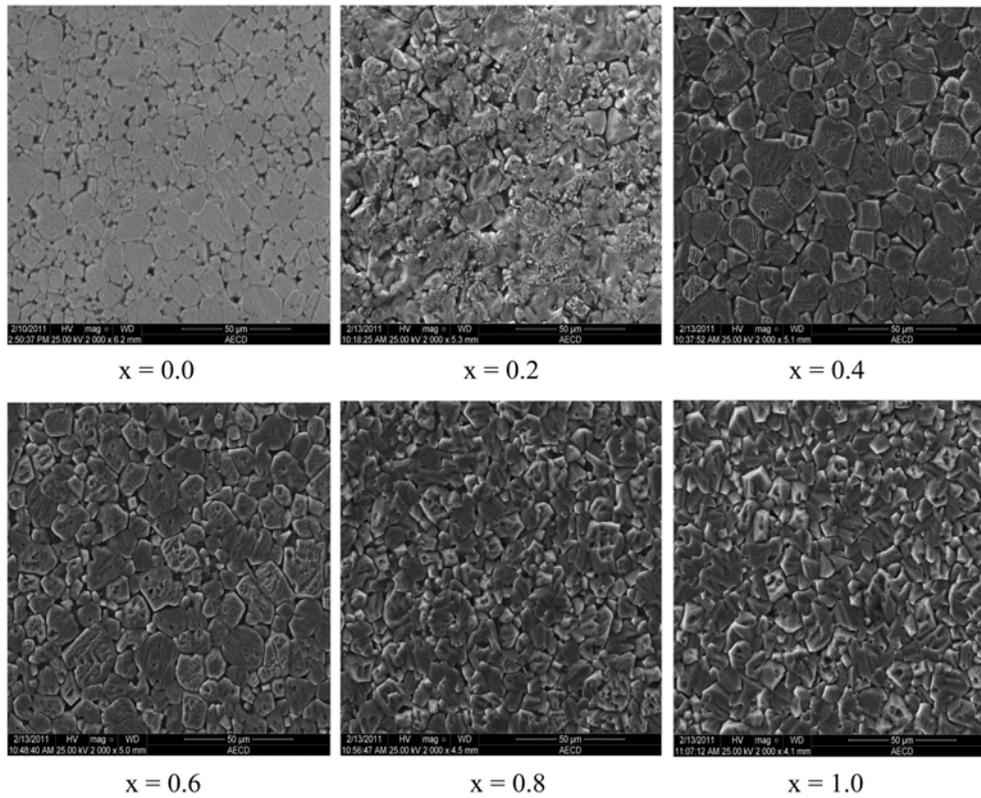


Fig. 4. SEM images of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ samples sintered at 1350 °C.

Microstructures

Magnetic and electrical properties sensitively depend on the microstructure of ferrites. Between the grain size and porosity of microstructures, the grain size is more important parameter affecting the magnetic properties of a ferrite. Grain growth is closely related to the grain boundary mobility. Recrystallization and grain growth involve the movement of grain boundaries. The grain growth being a result of interparticle mass transport, appears to be dominated by the bimodal diffusion mechanism [13, 14], of lattice and grain boundary diffusion. Scanning electron micrographs (SEM) of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ sintered at 1350 °C are shown in Fig. 4. It is observed from the microstructures that the grain size increases with an increase in Mg^{2+} substitution up to $x = 0.4$. This may be explained as due to the fact that the melting point of MgO (2852 °C) is much higher than that of NiO (1960 °C) [15]. After that the grain size decreases with further additions of Mg which may be due to the fact that the Mg^{2+} does not favor grain growth when present in excess amounts. This result agrees with the result for Zn , Cd , Cu substituted ferrites [16, 17]. For the samples with small grains, pores are found at the grain boundaries.

For the samples with large grains, the majority of pores are trapped inside the grains at large distance from the grain boundaries, which affects the value of permeability, resistivity and density [18].

Curie temperature (T_C) measurement

The Curie temperature (T_C) is a basic quantity in the study of magnetic materials. It corresponds to the temperature at which a magnetically ordered material becomes magnetically disordered, i.e. becomes paramagnetic. The Curie temperature also signifies the strength of the exchange interaction between the magnetic atoms. Fig. 5 shows the variation of the initial permeability (μ') with temperature for the series of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). It is seen that the initial permeability increases with temperature up to the Curie temperature, T_C . This result could be explained according to the Globus *et al.* relation [19], which is given by:

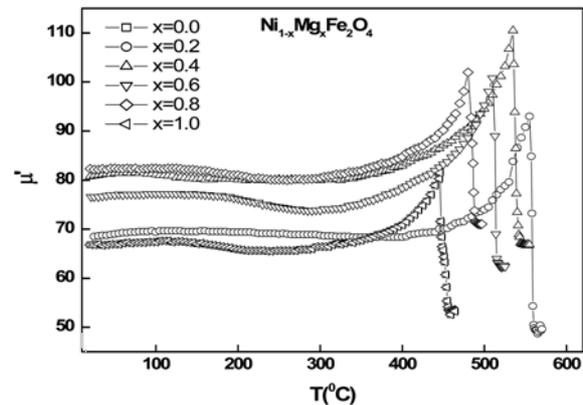
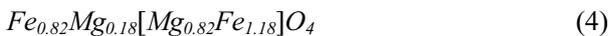


Fig. 5. Permeability vs temperature for different compositions of $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$.

$$\mu' = \frac{M_s^2 D}{\sqrt{\kappa_1}} \quad (3)$$

where D is the average grain size, M_s is the saturation magnetization and κ_1 is the anisotropy constant. The variation of μ' with temperature can be expressed as follows: the anisotropy constant (κ_1) and saturation magnetization (M_s) usually decrease with an increase in temperature. It is known that the anisotropy constant usually decreases much faster with temperature than saturation magnetization [20] which leads to the increase in μ' . The maximum value of μ' just below the Curie temperature (T_C), is a manifestation of the Hopkinson peak which is attributed to the minimization of anisotropy energy with temperature. Beyond this peak value μ' , the initial permeability sharply falls to a very low value indicating the ferro-paramagnetic phase transition. T_C has been taken as the temperature at which a sharp fall of the permeability is observed i.e. where $d\mu'/dT$ attains its maximum value [21]. The sharpness of the fall of permeability indicates the homogeneity and the single phase of the samples, which have also been confirmed by X-ray diffraction by our previous XRD experiments.

Fig. 6 shows the concentration dependence of T_C of $Ni_{1-x}Mg_xFe_2O_4$ system. It is observed that T_C decreases with Mg content. This decrease may be explained by a modification of the A-B exchange interaction strength due to the change of the Fe^{3+} distribution between A and B sites when Mg is substituted for Ni. The basic magnetic properties of the $NiFe_2O_4$ system originate from Ni^{2+} ions only in the octahedral B-sites since Fe^{3+} ions are distributed equally in both the A and B-sites. It is known that a Mg-ferrite is a spinel with inversion degrees of about 0.8 [15], with the following cation distribution:



where the brackets denote B-sites. Thus a small amount of Mg occupies the tetrahedral A-site while a larger amount occupies the octahedral B-sites. In such a

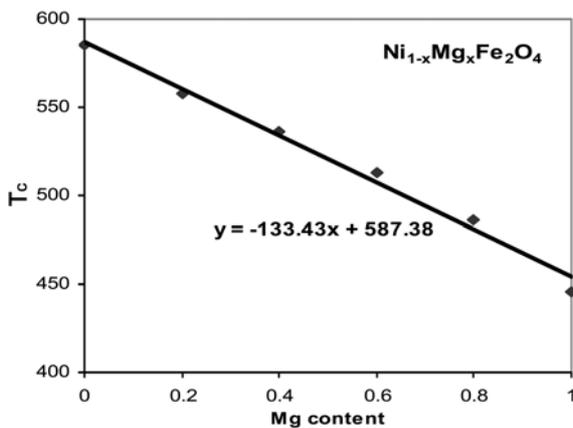


Fig. 6. Variation of the Curie temperature (T_C) with Mg content.

situation J_{AA} becomes weaker resulting in the weakening of the strength of the J_{AB} exchange interactions, which reduces the Curie temperature, T_C [22]. A linear least square fitting of the Curie temperature with x , gives an empirical relation for the whole $Ni_{1-x}Mg_xFe_2O_4$ system as follows:

$$T_C(x) = T_{C0} - 133.43 x \quad (5)$$

where T_{C0} is the Curie temperature of the pure Ni ferrite and $T_C(x)$ corresponds to the Curie temperature of any composition having a Mg content. From this empirical relation, the T_C of pure $NiFe_2O_4$ and $MgFe_2O_4$ are found to be 587 °C and 454 °C, respectively. Our experimental result is 585 °C for $NiFe_2O_4$ which is very close to the literature value 590 °C and 446 °C for $MgFe_2O_4$ which is very close to the literature value 440 °C [15].

Complex initial permeability

Fig. 7 shows the variation of the initial permeability spectra as a function of the Mg content. It is noticed that the real part of the initial permeability (μ') decreases with increasing Mg^{2+} substitution in $Ni_{1-x}Mg_xFe_2O_4$ samples sintered at 1350 °C. However the decrease in μ' with the increase of Mg content was not consistent with the variation of microstructures shown in Fig. 4.

According to the Globus and Duplex model [23], the static permeability and their product are microstructurally dependent. Ferrites with large grains are preferred to high permeability values because of the contribution of the domain wall motion. A decrease in the grain size results in a decrease in the number of domain walls in each grain. Moreover the decrease in initial permeability is closely related to the densification of the sample. A decrease in the density of ferrites not only results in an increase of the demagnetizing field due to the presence of pores but also reduces the spin rotational contribution, which in turn decreases the permeability [24, 25]. Therefore the decrease of the initial permeability of Ni-Mg ferrites with the increase of the Mg content was attributed to the decrease of bulk densities.

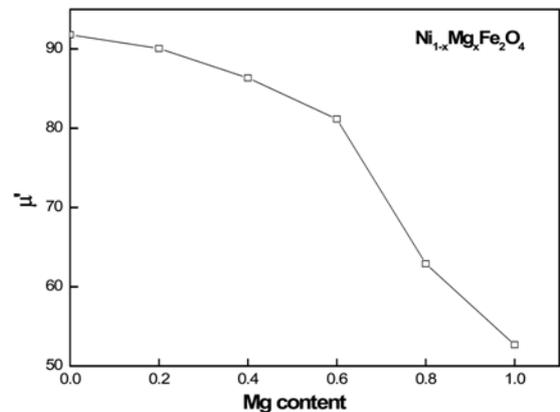


Fig. 7. variation of initial permeability (μ') with Mg content.

Conclusions

The presence of Mg ions causes appreciable changes in the physical and magnetic properties of the Ni-Mg ferrites. XRD results indicate a single phase of the pure cubic spinel structure. The lattice parameter increases with an increase of the Mg content. The bulk density and X-ray density are found to decrease linearly with increasing Mg content in the mixed Ni-Mg ferrite system. The grain size increases up to $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{Fe}_2\text{O}_4$ and decreases with further additions of magnesium. The Curie temperature decreases linearly with increasing Mg content. The initial permeability decreases with increasing Mg content.

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