

THE EFFECT OF VACANCIES ON SOME MAGNETIC PROPERTIES OF IRON - DEFICIT (NiO)_x(ZnO)_y(Fe₂O₃)_z SYSTEM

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ABSTRACT

The effect of iron deficiency of Ni_{0.30+2X}Zn_{0.70}Fe_{2-2X}O_{4-4X} with X = 0.00, 0.01, 0.02, 0.03 and 0.04 were carefully studied. High purity (99.992%) starting oxides were used and toroidal samples were prepared by using a conventional oxide-mixing technique. X-Ray Diffraction analysis of the iron deficit samples identified single phase ferrite. Grain size of 31.8µm and lowest theoretical porosity, 0.78%, for sample with 0.47 mole fraction of iron oxide was obtained. It is speculated that cationic and anionic vacancies are sufficiently formed for the diffusive transportation of metal ions to occur for the sample. However, sample with 0.46 mole fraction of iron oxide gave the highest saturation induction, 2757 Gauss as well as highest Curie temperature (5000C) due to stronger superexchange interaction.

INTRODUCTION

Extensive investigation is continuing on soft magnetic materials for their uses mainly on the radio frequencies region. They have been studied for several decades due to their wide range of applications in the field of telecommunications, audio and video electronics, power transformers, EMI suppression and many others involving electrical signals with frequencies normally not exceeding a few hundreds megahertz. Nickel zinc ferrite cores are commonly used for high frequency applications. As such, obtaining high density cores, which requires careful optimisation of both intrinsic and extrinsic factors is vital. We know that the departure from stoichiometry could affect the materials transport during solid-state reaction, which depends greatly on the vacancies concentration [1]. As such, we tried to obtain an effective value of ironoxide mole-fraction in samples with iron deficit composition to optimise the magnetic properties.

EXPERIMENTAL PROCEDURE

This work premise concerns the fabrication and characterisation of a series of $(\text{NiO})_X + 0.15(\text{ZnO}) + 0.35(\text{Fe}_2\text{O}_3) + 0.50 - X$ with $X = 0.00, 0.01, 0.02, 0.03$ and 0.04 . Creation of cationic and anionic vacancies to sufficiently aid diffusive transportation of metal ions with relative ease during sintering was done. It is believed that the cationic vacancies could affect the density of samples and thus profoundly affect the magnetic properties, such as the saturation induction and curie temperature of the fabricated samples. The structural and microstructural properties of the fabricated samples were investigated using X-Ray diffraction and scanning electron microscopy (SEM). All the samples were prepared via conventional method. $\text{Ni}_0.3\text{Zn}_0.7\text{Fe}_2\text{O}_4$ was sintered at 13500C for 10 hours, whereas all the non-stoichiometry samples were sintered at 13000C for 10 hours. XRay measurements were carried out in Siemen D5000 machine using $\text{Cu}\alpha$ radiation, with $\alpha = 1.5418\text{\AA}$. The scanning speed of the counter counter is 2_permin . Microstructure evolution of the sintered body was systematically done by using Scanning Electron Microscopy (SEM), JOEL-MSZ 6400 machine. The saturation induction values were obtain form hysteresis graph (Walker Scientific) where as the density measurements were obtained from the Archimedes principles.

RESULTS AND DISCUSSION

XRD patterns of all the compositions indicate complete spinel formation, as no lines of individual oxides were seen. All the compounds of the system crystallised out with cubic structure.

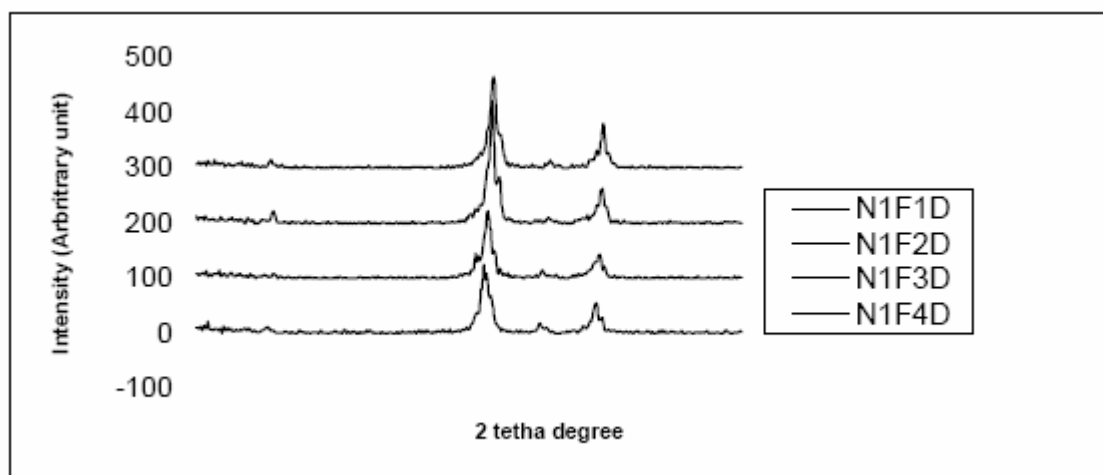


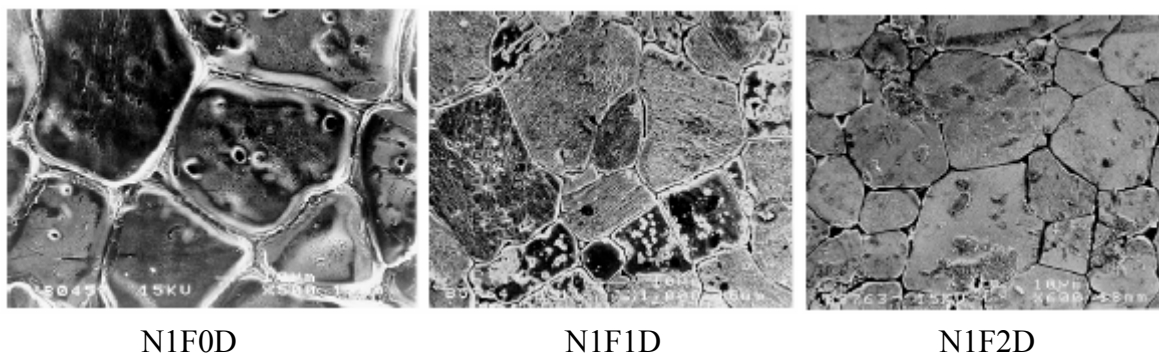
Figure 1: X-Ray Diffraction patterns for samples N1F0D, N1F1D, N1F2D, N1F3D and N1F4D

The fact that ferrites are extremely process sensitive and hence microstructure dependent is well known. The grain size, porosity and grain boundary phase of ferrites have great influence on the domain wall width, domain structure, and domain wall mobility [1,4]. A strong influence of vacancies on the final density and microstructure are observed.

Table 1: Theoretical density / vacancies and experimental properties for samples N1F0D, N1F1D, N1F2D, N1F3D and N1F4D

Sample	N1F0D	N1F1D	N1F2D	N1F3D	N1F4D
Composition	X=0.00	X=0.01	X=0.02	X=0.03	X=0.04
Vacancies (Theoretical)	0.00	0.16	0.32	0.48	0.64
Density (Theoretical) g/cm ³	5.2818	5.2442	5.2066	5.1691	5.1315
Density (Experimental) g/cm ³	5.2198	5.0889	5.0450	5.0899	5.0905
% Porosity (Theoretical)	1.17	2.96	3.10	1.53	0.78
Average Grain Size (μm)	75.2	41.8	48.3	31.2	28.2

Referring to Table 1, it is obvious from the theoretical calculations that the density drops with the increasing vacancies assuming the vacancies occur only on site B of the spinel structure. However, there is an increase in density for samples N1F3D and N1F4D. The increase of density for these samples could be due to the sufficient space or vacancies for an effective transportation of metal ions. The spinel lattice is primarily considered as a lattice of close-packed oxygen ions and thus metal transport depends strongly on the anionic vacancies [2] concentration. However, due to the iron deficiency adopted in this work, increasingly cationic vacancies are formed. Metal ions are speculated to be transported along both, the anionic and cationic vacancies, along the grain boundaries into the pores. Observing the microstructure of N1F3D and N1F4D, it is clear that the grains of both the samples are clear, small and dense compared to the other samples.



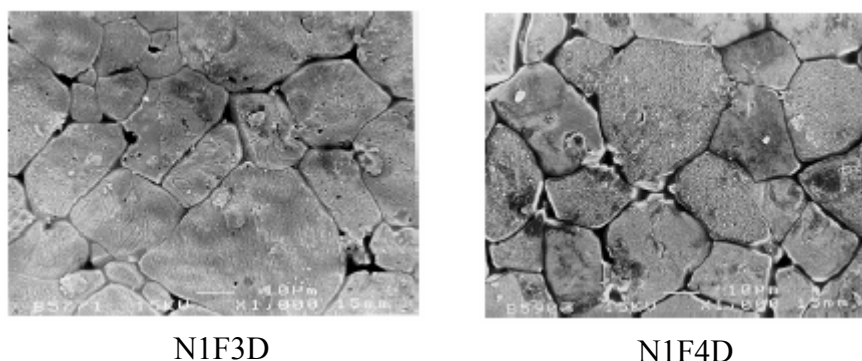


Figure 2: Micrographs of sintered samples N1F0D, N1F1D, N1F2D, N1F3D and N1F4D taken by the Scanning Electron Microscopy (SEM)

Observing Figure 2, sample N1F0D gives large grain size, $75.2\mu\text{m}$, with a few intragranular pores. This is due to the higher sintering temperature as compared to the non-stoichiometric samples. Sample N1F2D gives the lowest percentage of theoretical porosity value 0.32 % as well as homogeneous grain size, compared with N1F3D and N1F4D.

With rise in temperature, increasing thermal agitation weakens the strong directionality of the moments and there is a steady decrease in the net magnetic moments. This critical temperature, T_c , where a material behaves paramagnetic is shown in Table 2 below. In this work, there is an increase in Curie temperature as more vacancies being created. This could be due to the better transportation of metal ions and thus form a better spinel phase. As such, more vacancies are the reason to the better formation of ferrite phase and thus stronger superexchange interaction.

Table 2: Curie temperature, temperature coefficient and saturation induction for samples N1F0D, N1F1D, N1F2D, N1F3D and N1F4D

Sample	Curie temperature(K)	Temperature coefficient (1/K) ppm	Saturation Induction (kGauss)
N1F0D	417	18.6	1926
N1F1D	462	0.89	2276
N1F2D	464	0.08	2141
N1F3D	465	0.42	1901
N1F4D	500	0.43	2757

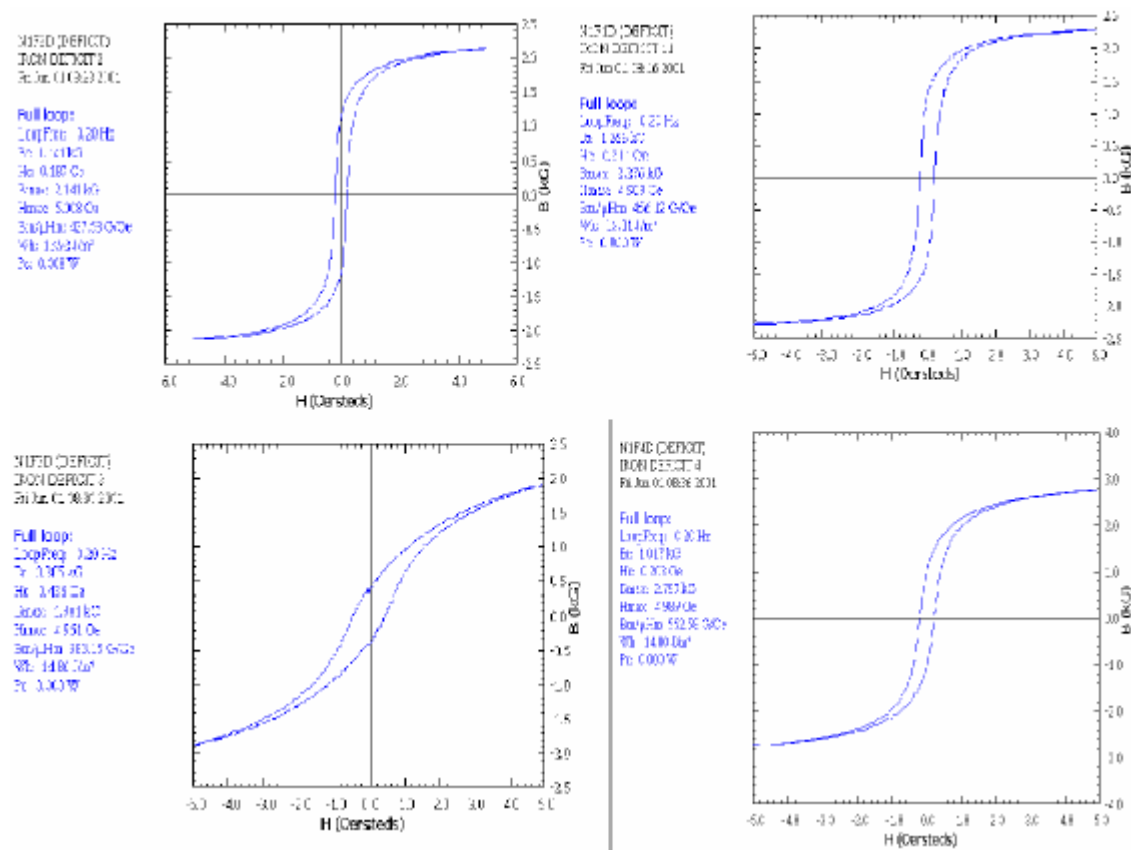


Figure 3 : Hysteresis Loop of Samples N1F1D, N1F2D, N1F3D and sample N1F4D

Temperature coefficient is an important technical parameter. All the non-stoichiometry samples give lower temperature coefficient, that is in the order of one to two (Table 2). This is a strong indication that these samples are stable towards temperature and thus has stronger superexchange interaction. The increment of NiO content with the increasing of Fe₂O₃ is supposed to result in a fall of saturation induction. This rests on the fact that Ni²⁺ gives 2.4 μB and Fe³⁺ gives 4.0 μB [4,5]. There is general trend of decreasing saturation induction up to sample N1F3D before a vast increase of the value for sample N1F4D (Table 2). Interesting however, is the vast increase of saturation induction value for sample with the most iron-deficit adopted. When the deficit amount of Fe₂O₃ with the increasing NiO is employed, it could be speculated that the more occupancy of Ni²⁺ in the B site with less Fe³⁺ ions reside the A site resulting in an increased net magnetic moments. Having closer look at sample N1F4D, it is obvious that this sample exhibit a very homogeneous microstructure (Plate 4) with smallest grain size and least theoretical porosity (Table 1). It could be speculated that saturation is done easily without much constrain. The domain structure is regular, without much pinning centers. The crystal does not contain much compositional inhomogeneities, non-magnetic inclusions such as voids and second phase and thus is not subjected to random mechanical stress.

CONCLUSION

It can be concluded that vacancies concentration in an iron-deficit $\text{Ni}_{0.30+2X}\text{Zn}_{0.70}\text{Fe}_{2-2X}\text{O}_{4-4X}$ can be considered a good route to obtain high density as well as good magnetic properties. The 0.47 mole fraction of iron-deficit NiZn ferrite composition gives the optimum number of vacancies for the transportation of metal ions during solid-state reaction which leads to stronger superexchange interaction and higher operating frequencies. Sample with 0.46 mole fraction of iron-deficit NiZn ferrite composition however, gave the highest saturation induction (2757 Gauss) and curie temperature (500 K).

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