

INFLUENCE OF TITANIUM SUBSTITUTIONS ON THE MAGNETIC PROPERTIES OF Ni-Zn FERRITES

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Ni-Zn ferrites with chemical formula $\text{Ni}_{0.65}\text{Zn}_{0.35+x}\text{Fe}_{1.99-2x}\text{In}_{0.01}\text{Ti}_x\text{O}_4$ where x value ranges from 0.000 to 0.125 in steps of 0.025 have been prepared by standard ceramic process. X-ray patterns confirm single phase cubic spinel structures and a slight modification of the lattice constants. Bulk densities of the samples have been measured by Archimedes method and straddle between 93 and 95% of their theoretical limits. Magnetization and Curie temperature measurements were made on the samples. The samples have resulted relatively higher magnetizations through out the series. However, the variation in magnetization with the substituents' concentration is minimal initially and thereafter the magnetization decreases with every increasing step of concentration. Curie temperature has been found to decrease by about 25°C with each step of substitution. The results are discussed on the basis of Neel's molecular field theory taking into account the site preferences of various cations present in the system. Conclusions have been derived at the end towards distribution of ions over the tetrahedral and octahedral sites.

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1. Introduction

Ni-Zn ferrites continue to be the subject of intense investigation as they find large number of applications over a wide frequency range from a few kHz to several MHz. Properties of these materials are very sensitive to composition, impurity levels and preparation methodology. Several workers have studied these ferrites both on the basic properties and on the influence of various substitutions depending on the applications of interest [1,2,3,4,5,6]. In power electronics, the requirement of magnetic components with higher operating frequencies at higher induction levels is steadily increasing as the newer technologies demand miniaturized assemblies. Particularly, when the devices need materials with operating frequencies beyond 1 MHz, Ni-Zn ferrites have an edge over the other soft magnetic materials. Thus, an attempt has been made to investigate a high magnetization nickel-zinc ferrite composition with substitutions of indium and titanium with an aim to improve its magnetic properties. Simultaneously, minor quantity of indium is also substituted in all the compositions by considering its ability to lower the total loss by decreasing the anisotropy constant and magnetostriction considerably [7]. This paper reports the variations in saturation magnetization and Curie temperature of a Ni-Zn ferrite system as a function of composition and discusses the results in terms of the compositional modifications and the possible mode of occupation of the lattice sites by cations.

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2. Experimental details

Polycrystalline Ni-Zn ferrites with the formula $\text{Ni}_{0.65}\text{Zn}_{0.35+x}\text{Fe}_{1.99-2x}\text{In}_{0.01}\text{Ti}_x\text{O}_4$ where x value ranges from 0.000 to 0.125 in steps of 0.025 have been prepared by conventional ceramic preparation technique using the procedure described elsewhere [8]. Sintering of the samples was done at 1250 °C for 4 hours in air followed by natural cooling. X-ray studies confirm single phase spinel structure in all the samples. Characterization of the samples was done by comparing the measured values of lattice constant, Curie temperature and saturation magnetization of the composition $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$ prepared under similar conditions with the corresponding parameters of the same composition reported earlier [9] and are found in good agreement with each other. Bulk densities of the samples have been observed to be 93-95% of their theoretical limits. Magnetization measurements are made using a VSM using the fields up to 15 kOe. Curie temperatures are measured using an experimental set up designed and constructed in our laboratory.

2. Results and discussions

i) Variation of Curie temperature with composition x

The variation in Curie temperature (T_c) with x is shown in Fig. 1. The Curie temperature has been observed to decrease with increasing concentration of the substituent; the decrease being almost linear and is about 25 ± 3 °C for every increasing step of substitution. The decrease in T_c can be explained on the basis of strength of the exchange interactions. In the present study, the system is subjected to simultaneous substitutions of titanium and zinc. As Curie temperature depends on the chemical composition, the observed variation in Curie temperature with titanium concentration suggests that substituted ions significantly modify the exchange interactions. Since the titanium ions have preference for B-sites they are expected to occupy B-sites only and the B-sublattice gets diluted with the increase in their concentration. And simultaneously, since the additional zinc ions substituted along with titanium ions prefer A-sites, the A-sublattice also gets diluted. As a result, according to the Neel's molecular field theory [10] all the three magnetic exchange interactions get weakened with every step of substitution. This explains the pronounced decrease in Curie temperature with the increase in substitutes' concentration.

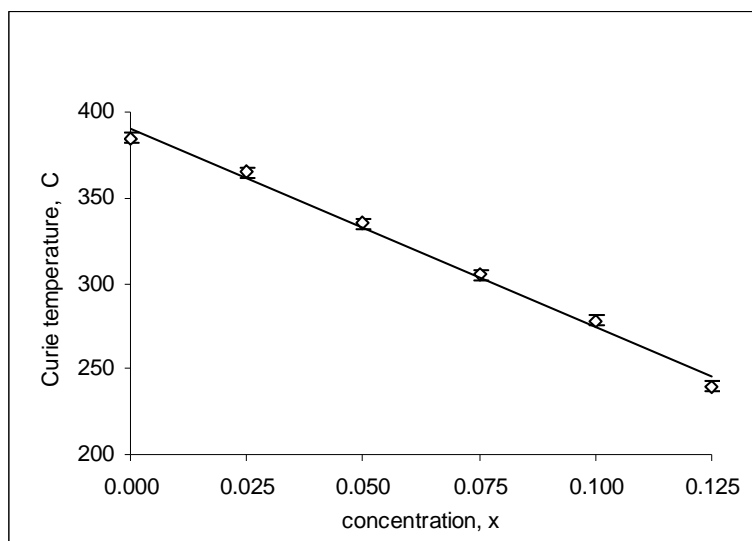


Fig. 1. Variation of Curie temperature, T_c with Ti^{4+} concentration in the system $\text{Ni}_{0.65}\text{Zn}_{0.35+x}\text{Fe}_{1.99-2x}\text{In}_{0.01}\text{Ti}_x\text{O}_4$.

ii) Variation of saturation magnetization with composition x

The variation of saturation magnetization, M_s , with concentration of the substituent is given in Fig. 2. For the first step of concentration of titanium, the saturation magnetization value remains almost constant and for subsequent concentrations it decreases gradually from 80 emu/gm to 60 emu/gm. The observed variations in saturation magnetization with simultaneous substitutions of zinc and titanium can be explained as follows:

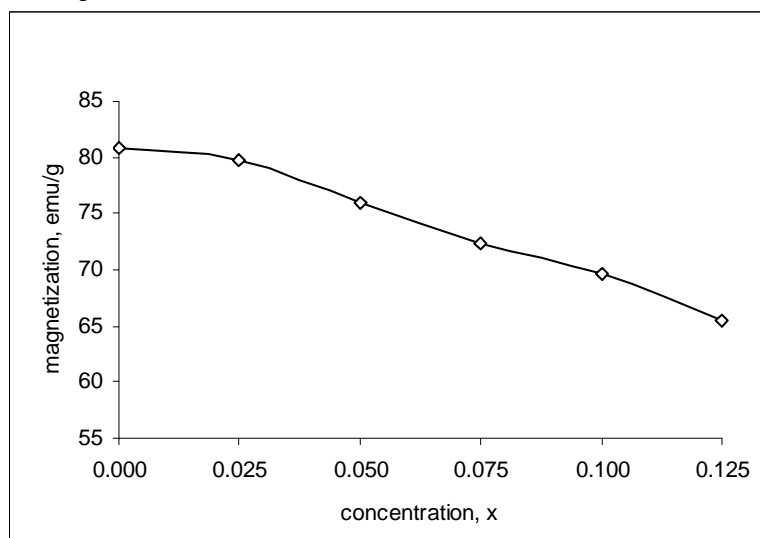
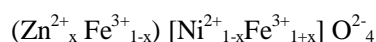


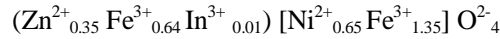
Fig 2. Variation of saturation magnetisation with Ti^{4+} concentration in the system $Ni_{0.65}Zn_{0.35+x}Fe_{1.99-2x}In_{0.01}Ti_xO_4$.

Since the substituted zinc ions in place of iron ions by occupying tetrahedral sites reduce the number of Fe^{3+} ions present in A-sites [11]. Similarly, since the titanium ions have specific preference for B-sites, they occupy B-sites only and consequently reduce the number of Fe^{3+} ions present in B-sites [12,13]. Thus, both the sublattice magnetizations get diluted and the net magnetization, being the difference between the both, should remain at the same value at least for initial concentration. But, the parallel substitution of minor quantity of indium ions, due to their initial preference for A-sites, by occupying A-sites, may force the equal number of Fe^{3+} ions there to move in to B-sites [7]. This may lead to a situation where the spins in A-sublattice could not keep all the spins in B-sublattice line up antiparallel to them. As a result, some of the spins in B-sublattice line up anti parallel with in the sublattice itself and the magnetization starts to decrease. However, magnetization contributions due to Fe^{2+} ions, that form during synthesis, reside in octahedral sites and prevent rapid fall of net magnetization at the initial concentration. The observed saturation magnetization value for the first step of substitution is in accordance with this. And for the subsequent concentrations, the increased dilution of A-sublattice with zinc occupation in A-sites forces the B-B interaction to enhance and as a result the magnetization is decreased gradually with every step of substitution. However, as the titanium ions are simultaneously entering B-sites in place of the Fe^{3+} ions they might be preventing the rapid decrease in magnetization. The explanation of the dependence of the saturation magnetization is in accordance with those concerning the resistivity dependence on the concentration of the TiO_2 additions, the results of which will be communicated separately.

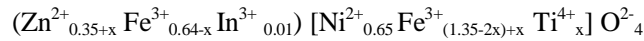
Based on the above discussion, the cationic distribution of the system could be written as [14]:



Since indium ions have initial preference for A-sites, the distribution for the basic composition is as follows:



As the additional zinc ions exclusively occupy A-sites and titanium ions have preference to occupy B-sites, the cation distribution in the system can be written as



3. Conclusions

Saturation magnetization and Curie temperature measurements on the samples indicate that there is a decrease in the strength of the exchange interactions due to nonmagnetic substitutions. Because of the specific site preferences of zinc and titanium ions for tetrahedral and octahedral sites, respectively, and corresponding dilution of both A- and B-sublattice magnetizations simultaneously with each step of substitution, the magnetization values were observed to be relatively higher throughout. However, for the confirmation of the site occupancy of titanium ions a Mössbauer spectroscopic study should be carried out on these samples. The information obtained from such study would provide a clear picture regarding the influence of substituted cations in these ferrites.

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