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X-ray and magnetic properties of manganese substituted Ni-Zn ferrites

B. PARVATHEESWARA RAO[a,b], CHONG-OH KIM[b*], CHEOL-GI KIM[b], O. F. CALTUN[c]
[a]*Department of Physics, Andhra University, Visakhapatnam 530003, India*
[b]*Deapartment of Materials Engineering, Chungnam National University, Daejeon, Korea*
[c]*Faculty of Physics, A.I. Cuza University, Iasi, 700506 Romania*

$Ni_{0.35}Zn_{0.65-x}Mn_xFe_2O_4$ ferrite system with x varies from 0.00 to 0.25 in steps of 0.05 has been prepared by conventional ceramic technique. The samples were sintered at 1250 °C for 4 hours in air atmosphere followed by natural cooling. X-ray diffraction patterns of all the samples exhibit all the major peaks concerned to the cubic spinel structure. Lattice constants were estimated using high angle x-ray peaks. The variation of lattice constant with manganese concentration follows the similar trend as that of percent porosity. Though the manganese ions with 5 μ_B are substituted in place of non-magnetic zinc ions, the saturation magnetization of the system is recorded a continuous increase through out the range of substitutions. Curie temperature of the system is also found to increase from 266 ^oC (x=0.00) to 372 ^oC (x=0.25) with the increase in manganese content. Smooth coercivity variation suggests better structural homogeneity. The results are discussed in light of the distribution of magnetic cations.

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1. Introduction

Ni-Zn ferrites possess several interesting properties that make them suitable for a large number of applications. They are used as transformer cores, antenna rods, inductors, deflection yokes, recording heads, etc. By adjusting the nickel-to-zinc ratio, their properties can be fine tuned to suit over a wide frequency range. Thus, these ferrites are considered as most versatile and they are being used in electronic industry in large quantities.

Several efforts were made earlier to enhance the basic properties of Ni-Zn ferrites by substituting nonmagnetic cations of different valence. It has been observed that the trivalent substitutions in these ferrites modify the magnetic properties [1]. The tetravalent substitutions have been found to improve the electrical properties while degrading the magnetic performance [2-3]. Recently, additions of pentavalent ions are reported to be effective in minimizing the power loss and thereby making these materials as potential candidates for high frequency power applications [4]. However, substitutions of divalent ions in place of either Ni or Zn ions in these systems have received little attention. Particularly, no data was available on systematic replacement of diamagnetic zinc ions by ferromagnetic Mn ions. There were some studies on the influence of Mn substitutions by replacing either Ni or Fe ions in Ni-Zn ferrites [5-6]. In these studies too, though the properties got modified, the role of the Mn ions in modifying the properties was not established satisfactorily. The Mn ions were largely assumed to reside in the spinel lattice either as trivalent or tetravalent. Further, the reports concerning the presence of Mn ions in divalent state are also not cohesive [7-8]. One study reported degradation of electromagnetic properties due to the presence of Mn^{2+} ions, while the other found enhanced magnetic response. Therefore, it is felt necessary to conduct a fresh study on the substitutions of Mn ions in Ni-Zn ferrites. Also, it is aimed at studying the influence of Mn ions when replacing nonmagnetic Zn ions as there is little work reported to this effect. This paper reports and analyzes the influence of Mn substitution on the variations of porosity, lattice constant, saturation magnetization and Curie temperature of Ni-Zn ferrites.

2. Experimental details

Polycrystalline Ni-Zn ferrites with the formula $Ni_{0.35}Zn_{0.65-x}Mn_xFe_2O_4$, where *x* takes the values ranging from 0.00 to 0.25 in steps of 0.05, have been prepared by conventional ceramic technique. Reagent grade chemicals of NiO, ZnO, Fe_2O_3 and $MnCO_3$ powders in stoichiometric proportions were wet ground homogeneously in methanol medium and calcined at 900 ^oC for 4 hours to obtain the spinel phase. The calcined powders were again wet ground and dired for granulation using 8% poly vinyl alcohol as binder. The powders were then pressed to form cylindrical shaped pellets and sintered at 1250 °C for 4 hours in air atmosphere. After the sintering, the furnace was switched off and allowed the samples to cool naturally. X-ray diffraction patterns of the samples confirm single phase cubic spinel structures in all the samples, and the sample densities were approximately 91-94% of their theoretical limits. Using the theoretical and experimental density data, porosity and lattice constant of the samples were estimated. Curie temperature measurements were made using the arrangement described by Soohoo [9]. Saturation magnetization was measured using vibration sample magnetometer. The measurements were carried out at room temperature only.

3. Results and discussion

Variations of porosity and lattice constant of $Ni_{0.35} Zn_{0.65-x} Mn_x Fe_2 O_4$ with Mn concentration are shown in Fig. 1. The initial concentration of Mn has contributed to obtain less porosity and thereafter the porosity varies little with the Mn concentration. However, all the Mn substituted samples exhibited lesser porosities compared to the basic Ni-Zn ferrite sample. These phenomena seem to be related to the improved homogeneity when Mn is substituted. In general, excess content of metal oxides in the form of insoluble secondary phases, liquid phases contributing to either slow or rapid densification generate increased pore volumes and demagnetizing fields [10]. Besides, inhomogeneities in the constituent metal oxide particles in synthesis add up to increase the defects and pore volumes in the final products. Contrarily, the lesser porosities in the present study indicate that the Mn ions are completely dissolved and entered the spinel lattice. The rather low porosity of the sample at x=0.05 may be attributed to extremely high degree of structural homogeneity of that sample.

The curve depicting the variation of lattice constant with Mn concentration also resembles that of porosity variation. However, except for the sample at x=0.05, the lattice constant values of all other samples are larger than that of the basic Ni-Zn ferrite composition. In the present study, the Mn ions with larger ionic radii of 0.97 Å, if they enter the lattice as Mn^{2+} only, are substituted to replace the Zn ions with relatively smaller ionic radii of 0.82 Å. Therefore, the lattice can be continuously expected to enlarge as more and more Mn is introduced in the system provided there is no change in the valence states of the cations involved. A previous study under similar synthesis conditions has, however, reported appreciable zinc loss and thereby a change in valence states of the cations present in order to maintain the charge neutrality [11]. The observed lower value of lattice constant for the sample at x=0.05 is thus attributed to the zinc loss and also to the presence of Mn^{3+} ions with smaller ligands apart from Mn^{2+} ions. The high sensitivity of Mn to the sintering temperature also favours it to react with the furnace atmosphere and exist simultaneously in different valence states [5]. Once the charge is balanced, the Mn would subsequently go to the lattice mostly as Mn^{2+} ions. This is confirmed by the higher values of lattice constant for higher concentrations of manganese.

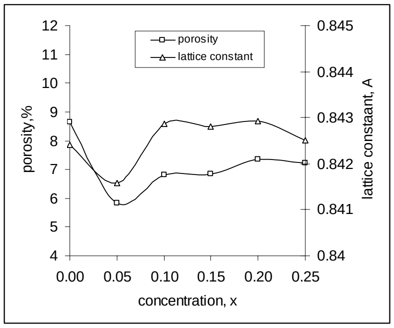

Fig. 1. Variation of % porosity and lattice constant with Mn concentration of $Ni_{0.35} Zn_{0.65-x} Mn_x Fe_2 O_4$.

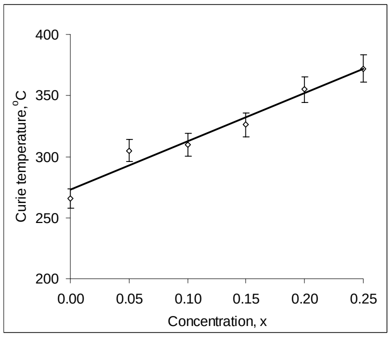

Fig. 2. Variation of Curie temperature with Mn concentration of $Ni_{0.35} Zn_{0.65-x} Mn_x Fe_2 O_4$.

Variation of Curie temperature with Mn concentration is shown in Fig. 2. There observed a continuous increase in Curie temperature with each step of substitution. Obviously, the exchange interactions between magnetic ions would increase with both the density and magnetic moment of the magnetic ions. As the diamagnetic zinc ions are replaced by ferromagnetic Mn ions with 5 μ_B in the present system, the total numbers of magnetic ions involved in exchange interactions increases continuously with each step of substitution and thus strengthen the A-B exchange interactions and support the increase in Curie temperature.

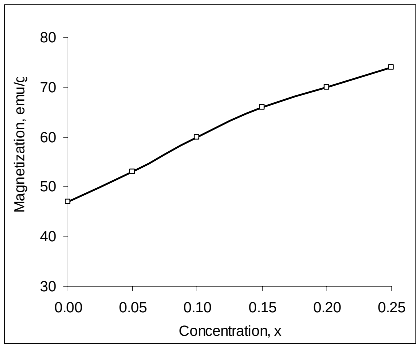

Fig. 3. Variation of saturation magnetization with Mn concentration of $Ni_{0.35} Zn_{0.65-x} Mn_x Fe_2 O_4$.

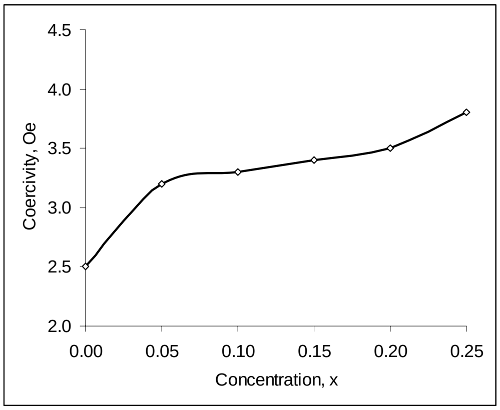

Fig. 4. Variation coercivity with Mn concentration of $Ni_{0.35}Zn_{0.65-x}Mn_xFe_2O_4$.

Variation of saturation magnetization with Mn concentration is shown n Fig. 3. The magnetization is observed to increase continuously throughout full range of substitutions. Before explaining the observed variation with Mn concentration, the possible cationic distribution scenario of the system prior to substitution can be described as follows: Based on the Mössbauer study [12] and with the basic assumption that all the iron in the system is in its trivalent state, the ionic distribution of the basic Ni-Zn ferrite composition, $Ni_{0.35}$ $Zn_{0.65}$ Fe_2 O_4 (for x=0), in the present study can be expressed as $(Zn_{0.65}^{2+} Fe_{0.35}^{3+})$ $[Ni_{0.35}^{2+} Fe_{1.65}^{3+}]$ O_4^{2-}. The cations within parenthesis occupy tetrahedral (A-) sites whereas those in square brackets occupy octahedral (B-) sites, respectively. Since iron content in A-sites is too small to hold all the iron spins in B-sites aligning antiparallel to the A-sublattice, there exists the possibility of B-B spin canting in B-sublattice for this composition. Further, according to the neutron diffraction studies conducted on Mn ferrite prepared by ceramic method [13] and wet chemical method [14], the occupation of Mn ions in A-sites is differed from 81% in the ceramic method to 33% in the wet chemical method. It implies that the Mn ions are highly sensitive to preparation methodology too in their preference for a particular lattice site.

If the Mn is substituted for Zn under the given scenario, the Mn ions need not necessarily occupy the A-sites only, but would occupy both the A- and B- sites according to their preference. The percentage of Mn that is occupied in B-sites would however force equal amount of iron to migrate into A-sites as there exist vacant sites due to the decreased zinc content. In such case, there are two possibilities under which the magnetization processes can be modified. Firstly, i) Since the amount of iron present in B-sites decreases while the amount of iron present in A-sites increases with each step of Mn substitution, the iron ions in A-sublattice becomes comparable to the iron ions in B-subllatice and would be able to maintain the antiparallel alignment between the sublattices, and thereby decreases the B-B spin canting and enhances the B-sublattice magnetization with every step of Mn substitution. And secondly, ii) though the magnetic moment of Mn^{2+} ions is same as that of Fe^{3+} ions, the strength in exchange interaction between Mn^{2+}-Fe^{3+} is small and therefore there will be a canting of spins of Mn^{2+} and of Fe^{3+} ions in the A-sublattice and thereby decreases the A-sublattice magnetization [8]. The process i) is directly effective to enhance the net magnetization of the system for lower concentrations of Mn by reducing the B-B spin canting, and process ii) is indirectly helpful to increase the net magnetization by self weakening of A-sublattice magnetization at higher Mn concentrations, wherein both the Mn and Fe are in sufficient amounts to trigger canting within themselves. The net result is increase in magnetization as the Mn concentration is increased and the observed variation is in agreement with the arguments made above.

Nevertheless, for the initial Mn concentration, as per reference 13, the 19% of 0.05 wt% Mn, which is expected to be in B-sites, is too small to reduce the B-B spin canting and to record increase in magnetization. But, the possible zinc loss at the sintering temperature due to volatilization causes Mn to form Mn^{3+} to that extent and these Mn^{3+} ions preferentially occupy B-sites only. This might have forced equal amount of iron to migrate to A-sites, thus responsible for reducing the spin canting in B-sublattice further and contributing to increase the net magnetization at this concentration.

Variation of coercivity with Mn concentration is shown in fig. 4. The variation is smooth for the whole range of Mn concentration. This implies that the motion of domain walls is not hindered by defects or secondary phase pinning points, which could be possible with the complete dissolution of Mn in the system and also with the improved structural homogeneity as discussed earlier.

4. Conclusions

In summary, the substitutions of manganese for zinc in Mn substituted Ni-Zn ferrites have displayed better structural homogeneity and improved magnetic performance. However, the variations of lattice constant and porosity are understood to point towards the simultaneous presence of Mn in two or more oxidation states. Increase in Curie temperature is explained by the increased density of magnetic cations with the addition of Mn^{2+} ions with higher magnetic momentum. Increase in saturation magnetization is explained based on the ionic distribution among lattice sites and different degrees of spin canting in different sublattices. The coercivity variation is believed to be another experimental evidence in support of the structural homogeneity of this system. Further study using SEM and chemical analysis would help to supplement the arguments made in this study.

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References

[1] G. F. Dionne, R. G. West, J. Appl. Phys. **61**, 3868 (1987).

[2] B. V. Bhise, M. B. Dongare, S. A. Patil, S. R. Sawant, J. Mater. Sci. Letts., **10** 922 (1991).

[3] B. Parvatheeswara Rao, K. H. Rao, K. Asokan, O. F. Caltun, J. Optoelectr. Adv. Mater.**6**, 959 (2004).

[4] S. Otobe, Y. Yachi, T. Hashimoto, T. Tanimori, T. Shigenaga, H. Takei, K. Hontani, IEEE Trans. Magn. **35,** 3409 (1999).

[5] H. Zhong, H. Zhang, J. Magn. Magn. Mater. **283**, 247 (2004).

[6] Z. Yue, J. Zhou, Z. Gui, L. Li, J. Magn. Magn. Mater. **264**, 258 (2003).

[7] J. H. Nam, W. G. Hur, J. H. Oh, J. Appl. Phys. **81**, 4794 (1197).

[8] A. K. Singh, T. C. Goel, R. G. Mendiratta, O. P. Thakur AND Chandra Prakash, J. Appl. Phys. **92**, 3872 (2002).

[9] R. F. Soohoo, Theory and Applications of Ferrites, Prentice-Hall, Engle-wood Cliffs, NJ (1960).

[10] J. G. M. de Lau, A. L. Stuijts, Philips Res. Rep. **21**, 104 (1966).

[11] B. Parvatheeswara Rao, K. H. Rao, J. Mater. Sci. **32**, 6049 (1997).

[12] J. M. Daniels, A. Rosencwaig, Can. J. Phys. **48**, 381 (1970).

[13] J. M. Hastings, L. M. Corliss, Phys. Rev. **104**, 328 (1956).

[14] J. Sakurai, T. Shinjo, J. Phys. Soc. Jpn. 23, 1426 (1967).

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[*] Correponding author: cgkim@cnu.ac.kr