CATION DISTRIBUTION IN $NI_{0.7}ME_{0.3}FE_2O_4$ (ME = ZN, CO AND MN)

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Abstract

$Ni_{0.7}Me_{0.3}Fe_2O_4$ (Me = Zn, Co and Mn) were synthesized through co-precipitation method. Cationic distribution for these ferrites was proposed on the basis of magnetization measurements and available occupancy of the substituent ions into the spinel lattice. Theoretical lattice constant calculations confirm the proposed cationic distributions were the correct ones.

Keywords: Magnetization, Cation distribution, Lattice constant

1. Introduction

Achievement of desired magnetic and electrical properties of ferrites is in general sensitive to the distribution of cations among tetrahedral and octahedral sites of the spinel lattice which intern depend on the method of processing. Though several mixed ferrite systems have been studied extensively, still there is ample of scope in understanding the modification in the properties of new sets of ferrites as well as the existing ones. Even a slight deviation in the quantity of cations distributed over both the sites poses a great variation in the properties of ferrites. Optimization in properties can be attained through a precise distribution of cations over the spinel lattice. Upon revision of field of ferrites, Nickel, Cobalt and Manganese containing ferrites seem to have a prominent impact in providing properties suited for a specific application. Understanding of distribution of cations is an essential aspect for obtaining a high-quality ferrite.

Many investigators have reported the distribution of cations in Ni-Zn ferrites as $Zn_x^{2+}Fe_y^{3+} \; Fe_{2-y}^{3+}Ni_{1-x}^{2+} \; O_4^{2-}$. Nickel ferrite is generally a complete inverse ferrite having a Neel-type of collinear arrangement of $(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4$. Van Uitert extensively investigated nickel ferrite by incorporating small amounts of manganese or cobalt in place of nickel and found marked improvement in electromagnetic properties [10]. Although there available a wide variety of simple ferrites in the early days of research, it is always desirable to prepare mixed ferrites with different metal ion concentrations to obtain important characteristics. For instance, in Ni ferrite, the values of magnetization and Curie temperature can be conveniently varied by adding zinc in suitable amounts. Though nickel-zinc ferrite system has been found in a wide variety of applications, recent technological developments focused on nickel-cobalt and nickel-manganese ferrite systems. Nickel-cobalt ferrites mainly found applications in high-density magnetic recording media and microwave devices because of their moderate saturation magnetization, high coercivity, mechanical hardness and chemical stability [11]. Nickel-Manganese ferrites have also attracted the attention of many researchers due to their colossal magnetoresistance effect. Mossbauer study indicates that $Ni_{0.5}Co_{0.5}Fe_2O_4$ system has inverse spinel structure with cation distribution as $(Fe^{3+})[Ni_{0.5}^{+}Co_{0.5}^{+}Fe^{+}]O_4$ [12]. From x-ray diffraction study, $Ni_{1-x}Mn_xFe_2O_4$ using Quiang-Min Wei et.al. [13] has been reported to belong to the family of mixed or partially inverse spinel ferrites. In another report [14] the same authors established that Ni^{2+} ions have strong preference to occupy octahedral site and Mn^{2+} ions to tetrahedral site; thus confirming the behavior of mixed ferrite. Cation distribution for $Ni_xMn_{1-y-x}Fe_{2+y}O_4$ has been proposed using thermodynamic method and the distribution was found to be in good with that obtained from X-ray diffraction study. To verify the structural behavior of nickel-cobalt
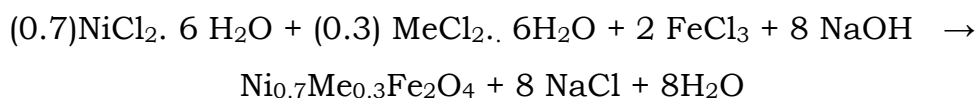
and nickel manganese ferrite systems belonging to inverse or mixed, much information has not been available in the literature.

The aim of the present work is i) processing of fine particles of cobalt containing ferrite samples $Ni_{0.7}Zn_{0.3}Fe_2O_4$, $Ni_{0.7}Co_{0.3}Fe_2O_4$ and $Ni_{0.7}Mn_{0.3}Fe_2O_4$ by co-precipitation method followed by annealing ii) study of crystallite size from X-ray diffraction and Curie temperature of the ferrites iii) determination of cation distribution from saturation magnetization measurements iv) calculation of the theoretical lattice parameter from the proposed cation distribution and comparison of theoretically estimated and experimentally obtained lattice parameters.

2. Experimental details

For the preparation of $Ni_{0.7}Me_{0.3}Fe_2O_4$ (Me = Zn, Co and Mn) through co-precipitation, high pure cobalt, zinc, nickel, manganese and iron chlorides were taken in stiochiometric proportions and made dissolved separately in minimum amount of deionized water according to the chemical formula.

$$(0.7)NiCl_2 . \ 6 \ H_2O + (0.3) \ MeCl_2 .. \ 6H_2O + 2 \ FeCl_3 + 8 \ NaOH \ \rightarrow$$
$$Ni_{0.7}Me_{0.3}Fe_2O_4 + 8 \ NaCl + 8H_2O$$

Thus prepared cationic solution were mixed intimately so as to obtain the required compositions and stirred intensely for 1 hr to improve homogeneity. The resulting solutions, precursors, subjected to constant heating at 60^oC under continuous stirring. At this stage the co-precipitating base, aqueous NaOH in required proportion was added slowly drop by drop to the precursor solutions till a massy precipitate was formed at the bottom of the reaction vessel. Washing of the precipitate was done several times with deionized water and finally with

acetone to remove the traces of water any. Pellets were prepared using 15 % polyvinyl alcohol under a uniaxial pressure of 10^5 psi. X-ray diffraction patterns of all the samples were recorded using Rigaku Miniflex X-ray diffractometer with Cu-Kα radiation (λ=1.5406 Å). Saturation magnetization was measured using Ponderometer method [4]. Curie temperature was determined with Soohoo method [5].

3. Results and discussion

X-ray diffraction patterns of the $Ni_{0.7}Me_{0.3}Fe_2O_4$ (Me = Zn, Co and Mn) powders confirmed the single phase spinel structure [fig 1(a)]. The average crystallite size of all the samples has been estimated using FWHM of each diffraction peak and Debye-Scherrer formula [6, 7]. In order to obtain FWHM, a non-linear least square fit has been constructed assuming experimentally obtained diffraction peaks obey Voigt function [fig 1(b)].
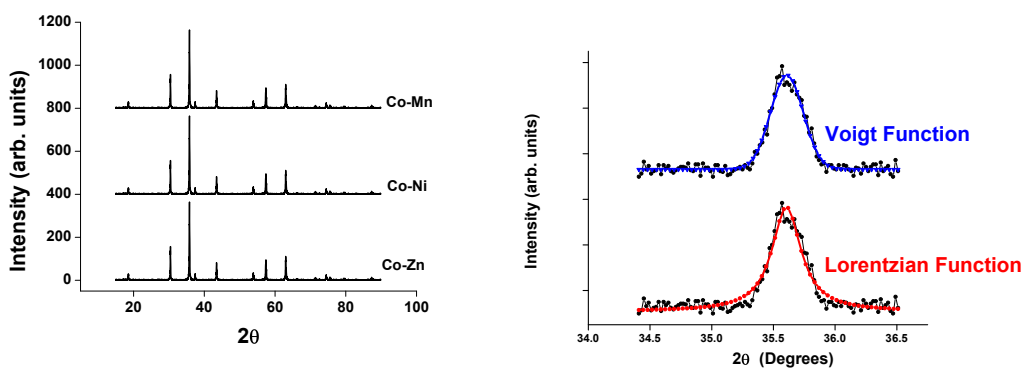

Figure 1: a) X-ray diffraction peaks b) Least squares fitting for a prominent (311) peak assuming either Lorentzian or Voigt function.

The value of average crystallite size is also estimated by constructing Williamson-Hall plots ($\frac{B\cos\theta}{\lambda}$ versus $\frac{\sin\theta}{\lambda}$) using the values of FWHM and incident angle θ corresponding to each diffraction peak. Extrapolation of these graphs provides the value of $\frac{B\cos\theta}{\lambda}$ corresponding to zero strain, the

reciprocal of which determines the crystallite size [fig. 2(a)]. Average crystallite size calculated from both the methods is found to be in good agreement and increasing with increasing ionic radii of substituted metal cation which might be attributed to entry of each ion into the lattice and variations in the rates of reaction for each specific ion [fig. 2(b)]. Similar tendency has been noticed in lattice constant, obtained from Nelson-Riley function [8].
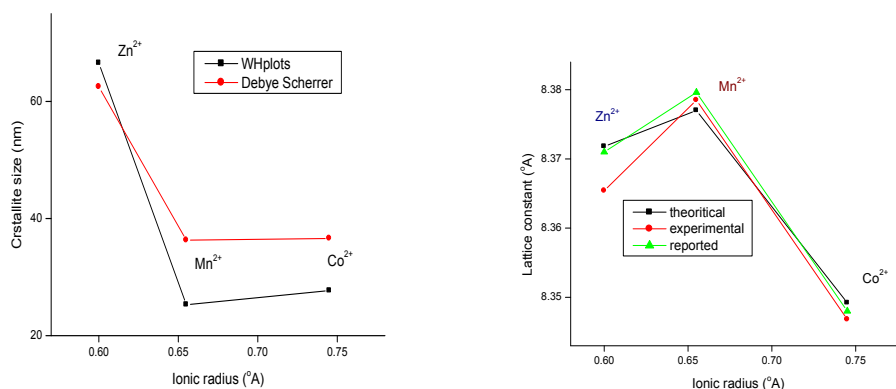

Figure 2: a) Average crystallite size and b) Lattice constant versus ionic radius

Figure 3(a) shows the variations in saturation magnetization with ionic radius of the dopant. The saturation magnetization of cobalt ferrite decreases with the partial replacement of Co^{2+} ions by Ni^{2+} ions because the magnetic moment associated with nickel ion is $2\mu_{\_}$, less than that of Co^{2+} ion (3μ). Moreover, nickel ions are known to occupy octahedral sites and cause decrease in the B-site magnetic moment. As the net magnetic moment of the sample is equal to the difference in B site and A-site magnetic moments, M_B-M_A, a decrease in overall magnetic moment of the sample is expected. This kind of explanation is valid provided the strongest A-B interaction persists among various cations existing on A and B sublattices.

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It is well known [9] that Zn^{2+} ions occupy tetrahedral sites, Ni^{2+} ions occupy octahedral sites and Mn^{2+} ions occupy tetrahedral sites. Co^{2+} ions are reported to occupy A-sites up to a maximum of 10 % in cobalt ferrite [10, 11] depending on the annealing temperature. From Mossbauer study of cobalt–zinc ferrite [1] it has been observed that the amount of cobalt at A-site decreases from 10 % with the increase of zinc content.

In case of Co-Zn ferrite system, non-magnetic Zn^{2+} ions are known to occupy tetrahedral (A) sites due to their strong preference and decrease the magnetic moment of A-sublattice and hence an increase in the total magnetic moment of the sample is predicted. Similar behaviour has been reported [12] in $Co_{1-x}Zn_xFe_2O_4$ system up to x = 0.4. The highest value of saturation magnetization for the composition $Co_{0.9}Zn_{0.1}Fe_2O_4$ [13] was noticed and explained the result on the basis of cationic distribution and their occupancy in specific sites. The substitution of Mn^{2+} for Co^{2+} produces changes in the value of saturation magnetization depending on the heat treatment. Mn^{3+} ions will have strong preference for the octahedral sites when Fe^{3+} in cobalt ferrite is replaced by Mn^{3+} [9]. On the other hand, Mn^{2+} ions will have stronger preference for the tetrahedral sites [10] if Co^{2+} is replaced by Mn^{2+}. In the present study the experimentally observed value of magnetization in Co-Mn ferrite is in accordance with the replacement of Co^{2+} ions by Mn^{2+}.
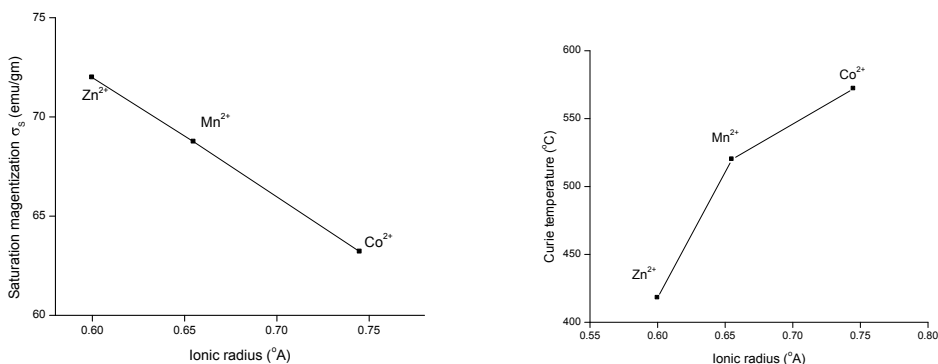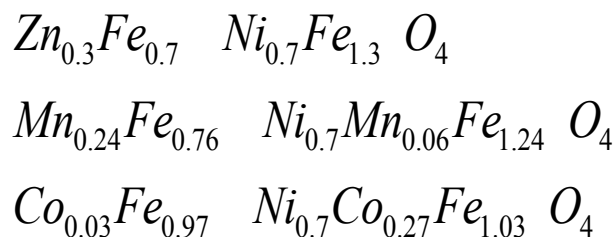

Figure 3: a) Saturation magnetization and b) Curie temperature versus ionic radius

Figure 3(b) shows the variations in Curie temperature. As is clear from the table, except Co-Mn ferrite the other two ferrite systems show less value of Curie temperatures than that of the cobalt ferrite. The observed variations in Curie temperature are explained on the basis of the super exchange interactions among the metallic cations distributed between the two sublattices. As described in saturation magnetization, the substitution of Ni^{2+} in place of Co^{2+} should decrease the magnetic interactions since the ion having less magnetic moment (Ni^{2+}) is replacing an ion having high magnetic moment (Co^{2+}). In case of Co-Mn ferrite, as Mn^{2+} ion magnetic moment (5μ) more than magnetic moment of Co^{2+} ion (3μ), the rise in magnetic interactions is generally expected which increase the Curie temperature. In case of Co-Zn ferrite system, the substitution of non-magnetic zinc in place of ferromagnetic cobalt leads to a decrease in Curie temperature owing to diminishing A-B super exchange interaction.

Cation distribution for these ferrites has been proposed on the basis of saturation magnetization measurements. In the present study, the occupancy amount of cobalt ions at tetrahedral sites has been chosen to be about 5% to provide the following better possible cationic distributions agreeable to experimentally observed number of Bohrmagnetons per molecule.

$$Zn_{0.3}Fe_{0.7} \quad Ni_{0.7}Fe_{1.3} \quad O_4$$

$$Mn_{0.24}Fe_{0.76} \quad Ni_{0.7}Mn_{0.06}Fe_{1.24} \quad O_4$$

$$Co_{0.03}Fe_{0.97} \quad Ni_{0.7}Co_{0.27}Fe_{1.03} \quad O_4$$

Besides providing the experimentally observed lattice constant, theoretical lattice constants have also been estimated using the following

formulae by proposing cationic distribution of metal ions in the spinel lattice.

$$r_A = \left(\quad \right)$$

$$r_B = \left(\quad \right)$$

$$a_{th} = \frac{\overset{\circ}{}}{3\sqrt{3}} \left[\qquad\qquad\qquad \right]$$

where r_A and r_B are radii of tetrahedral and octahedral sites respectively. R_0 is the radius of oxygen ion. u is oxygen positional parameter. For face centered cubic structure the value of oxygen parameter is 0.375. In the Co-Zn ferrite system the radii of Zn^{2+} and Co^{2+} ions are greater than the space occupied by the oxygen ions. This will cause distortion in the cubic lattice and therefore the oxygen parameter may differ from its usual value 3/8 [14].

Theoretical lattice constants corresponding to these ferrites have been calculated using the proposed cationic distributions. The calculated lattice constants are found to be in agreement with the experimentally observed and reported lattice constant values (Table 1).

Table 1: Theoretical, experimental and reported values of lattice constants

Composition	Proposed distribution (Å)	Experimental (Å)	Reported (Å)	Reference
$Ni_{0.7}Zn_{0.3}Fe_2O_4$	8.3718	8.3654	8.3712	[13]
$Ni_{0.7}Co_{0.3}Fe_2O_4$	8.3492	8.3468	8.3481	[12]
$Ni_{0.7}Mn_{0.3}Fe_2O_4$	8.3770	8.3785	8.3796	[14]

4. Conclusions

X-ray diffraction measurements confirmed the single phase spinel structure for all the ferrites and lattice constant has been measured by using Nelson-Riley function. Cation distribution for the compositions has been proposed on the basis of saturation magnetization values and the preferred site occupancy of the ions in the ferrite lattice. Confirmation of cation distribution has been done through theoretical lattice constant calculations. A good agreement between theoretical and experimental lattice constants has been found for all the compositions.

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