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Cation Distribution in $Mn_{0.7}Me_{0.3}Fe_2O_4$ (Me = Ni, Co and Zn)

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ABSTRACT

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

1. Introduction

Distribution of cations over tetrahedral and octahedral sites has been the subject of many researchers [1-4], since electrical, magnetic, structural and other properties of ferrite are strongly dependent on the arrangement of ions in the unit cell. The factors [5-6] which can influence the distribution of the metal ions over the A and B sites are their ionic radii, electronic configuration of the metal ions and the electrostatic energy of the spinel lattice. The understanding of cation distribution is an essential aspect for obtaining a high-quality ferrite for a specific application.

Many investigators have reported the distribution of manganese ions over tetrahedral and octahedral sites and the observations found to often conflicting. Through neutron diffraction study [7, 8], the distribution of cations in manganese ferrite was given as $\left(Mn^{2+}_{0.81}Fe^{3+}_{0.19}\right)\left[Mn^{2+}_{0.19}Fe^{3+}_{1.81}\right]O_4$ in which nearly 80% of manganese occupying tetrahedral sites. In $Mn_{1-x}Zn_xFe_2O_4$ system [9], Mn^{2+} and Fe^{3+} ions tend to occupy octahedral sites than tetrahedral sites. DH Le et. al. [10] concluded through Mossbauer study, Mn^{2+} ions tend to occupy B-sites at lower concentrations and A-sites at higher concentration. Krieble et. al. [11] studied $CoMn_xFe_{2-x}O_4$ system and observed the transfer of cobalt ions from octahedral sites to tetrahedral sites with an increase in manganese content at B-site. Basing on the oxidation state, Mn^{3+} ions have strong preference for octahedral sites when replacing Fe^{3+} ions in cobalt ferrite [8, 12] whereas Mn^{2+} ions tend to occupy tetrahedral sites [13] if Co^{2+} is replaced by Mn^{2+}. Similar observations have been mentioned in cobalt - manganese ferrite by Paulsen et. al.[14]. In $Ni_{1-x}Mn_xFe_2O_4$ using X-ray diffraction study Qiang-Min Wei et al., [15] reported that the system belonged to the family of mixed or partially inverse spinel ferrites. In another report [16] the same authors established that Ni^{2+} ions have strong preference to occupy B-site, whereas the Mn^{2+} ions having preference towards A-site. Cation distribution in $Ni_xMn_{1-y-x}Fe_{2+y}O_4$ has been proposed [17] using thermodynamic method and found to be in good agreement with the distribution obtained from X-ray diffraction study. Occupancy of a fraction of zinc ions to B-sites has been reported [18] in Mn-Zn nanoferrites synthesized by hydrothermal process.

The aim of the present work is i) processing of fine particles of cobalt containing ferrite samples $Mn_{0.7}Ni_{0.3}Fe_2O_4$, $Mn_{0.7}Co_{0.3}Fe_2O_4$ and $Mn_{0.7}Zn_{0.3}Fe_2O_4$ 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 $Mn_{0.7}Me_{0.3}Fe_2O_4$ (Me = Ni, Co and Zn) through co-precipitation, high pure cobalt, zinc, nickel, manganese and iron chlorides were taken in stoichiometric proportions and made dissolved separately in minimum amount of deionized water according to the chemical formula.

$(0.7)MnCl_2 . 4\ H_2O + (0.3)\ MeCl_2 .\ 6H_2O + 2\ FeCl_3 + 8\ NaOH \rightarrow Mn_{0.7}Me_{0.3}Fe_2O_4 + 8\ NaCl + 8H_2O$

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°C 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 [19]. Curie temperature was determined with Soohoo method [20].

3. Results and Discussion

X-ray diffraction patterns of the $Mn_{0.7}Me_{0.3}Fe_2O_4$ (Me = Ni, Co and Zn) 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 [21, 22]. 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)].

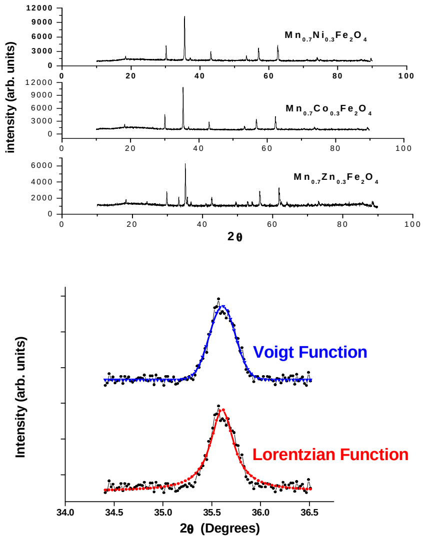

Figure 1: ***a) X-ray diffraction peaks b) Least squares fitting for a prominent (311) peak assuming either Lorentzian or Voigt function.***

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)]. The average crystallite size has also been obtained from full-width at half maximum (FWHM) of each X-ray diffraction peak by using the Debye-Scherrer formula. Average crystallite size calculated from both the methods is found to be in close 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. The observed trend of the lattice constant is in accordance with the increasing ionic radii of substituted metallic ions ($r_{Zn} > r_{Co} > r_{Ni}$).

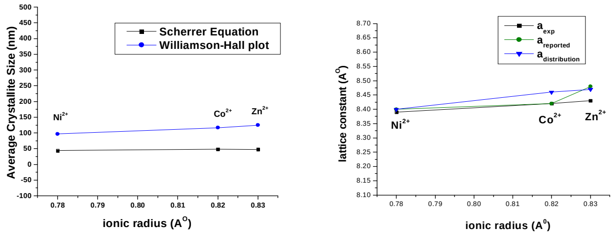

Figure 2: a) Average crystallite size and b) Lattice constant versus ionic radius

Figure 3(a) shows the variations in saturation magnetization with ionic radius of the dopant. The value of saturation magnetization of manganese ferrite is found to be 80 emu/g and its magnetization decreases with the substitution of Ni^{2+} ions in place of manganese. This is due to the less value of magnetic moment associated with nickel ion ($2\ \mu_B$) compared to that of Mn^{2+} ion ($5\ \mu_B$). Mn^{2+} ions have strong preference for tetrahedral sites in the spinel lattice where as nickel ions are known to occupy octahedral sites.

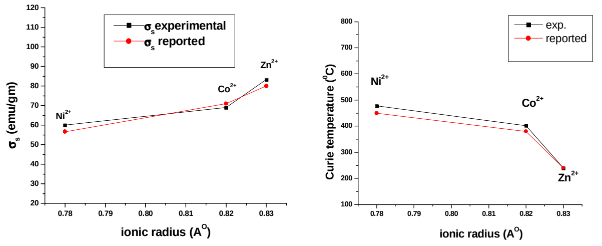

Figure 3: a) Saturation magnetization and b) Curie temperature versus ionic radius

Out of the total manganese content in Mn ferrite, it has been reported that [6] only 80% of the Mn^{2+} ions occupy A-site and the remaining manganese ions in B-site are replaced by the nickel ions causing a decrease in the B-site magnetic moment. As the net magnetic moment of the ferrite is equal to the difference of the both B and A-site magnetic moments, M_B-M_A, a decrease in the 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.

Substitution of cobalt ions in place of manganese results in the reduction of saturation magnetization slightly. This can be attributed to the occupancy of cobalt ions. It has been reported that [19] cobalt ions tend to occupy 20% for A-sites and the remaining 80% for B-sites in the spinel lattice. When manganese ions with magnetic moment 5 μ_B are replaced by Co^{3+} ions with magnetic moment 3 μ_B, decreases B-site magnetization. So the net magnetic moment decreases and hence the observed reduction in magnetization.

In case of zinc substitution, zinc ions have their usual tendency towards A-sites whereas manganese ions are distributed through both the sites. Replacement of A-site manganese with zinc ions decreases the magnetic moment the respective sublattice and hence the resultant magnetization, M_B-M_A, increases a bit consequently which has been noticed in the current study.

Figure 3(b) shows the variations in Curie temperature. As all the compositions containing constant amount of manganese at A-sites, the variation in T_C has been explained on the basis of the presence of other ions at A-site. In spinel structure each A-site ion has in its immediate surrounding 12 B-site neighbors and each B-site ion has 6 A-sites as immediate neighbors. In $Mn_{0.7}Co_{0.3}Fe_2O_4$, B-site ion is surrounded by cobalt and iron ions whereas in $Mn_{0.7}Ni_{0.3}Fe_2O_4$ sample the same sees iron ions as its neighbors. As we know the cobalt ion has less magnetic moment than iron ion and reduced amount of iron in $Mn_{0.7}Co_{0.3}Fe_2O_4$ sample along with cobalt are responsible for the lower of value Curie temperature compared to $Mn_{0.7}Ni_{0.3}Fe_2O_4$. In $Mn_{0.7}Ni_{0.3}Fe_2O_4$ ferrite, as B-site sees only nonmagnetic zinc environment drastic decrease in Curie temperature is observed.

It is well known [7, 9, 15] in mixed ferrite systems 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 tetrahedral A sites partially up to 5 mole % [10] in cobalt ferrite and cobalt substituted manganese ferrite [23]. On the basis of above site preference considerations the following distributions for the samples of the present study are proposed.

$$Mn_{0.7}Ni_{0.3}Fe_2O_4 \rightarrow \left(Mn^{2+}_{0.7}Fe^{3+}_{0.3}\right)\left[Ni^{2+}_{0.3}Fe^{3+}_{1.7}\right]O^{2-}_4$$

$$Mn_{0.7}Co_{0.3}Fe_2O_4 \rightarrow \left(Mn^{2+}_{0.7}Co^{2+}_{0.03}Fe^{3+}_{0.27}\right)\left[Co^{2+}_{0.27}Fe^{3+}_{1.73}\right]O^{2-}_4$$

$$Mn_{0.7}Zn_{0.3}Fe_2O_4 \rightarrow \left(Mn^{2+}_{0.7}Zn^{2+}_{0.3}\right)\left[Fe^{3+}_2\right]O^{2-}_4$$

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 in order to check the correctness of the proposed distribution.

$$r_A = \left(u - \frac{1}{4}\right) a_{th}\sqrt{3} - R_0$$

$$r_B = \left(\frac{5}{8} - u\right) a_{th} - R_0$$

$$a_{th} = \frac{8}{3\sqrt{3}}\left[\left(r_A + R_0\right) + \sqrt{3}\left(r_B + R_0\right)\right]$$

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. 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).

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.

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

Composition	Proposed distribution (A^o)	Experimental (A^o)	Reported (A^o)	Reference
$Mn_{0.7}Ni_{0.3}Fe_2O_4$	8.39	8.40	8.40	[24]
$Mn_{0.7}Co_{0.3}Fe_2O_4$	8.42	8.42	8.46	[25]
$Mn_{0.7}Zn_{0.3}Fe_2O_4$	8.43	8.48	8.47	[26]

5. References

[1] M.A. Willard, Y. Nakamura, D.E. Laughlin, M.E. Mechenry, *J. Am. Ceram. Soc.* 82, 3342 (1999).

[2] V. Montouillout, D. Massiot, A. Duoy, J.P. Coutures, *J. Am. Ceram. Soc.* 82, 3299 (1999).

[3] E. Kester, B. Gillot, *J. Phys. Chem. Solids* 59, 1259 (1998).

[4] MH Mahmoud, HH Hameh, AI Abdel-Mageed, AM Abdallah, MK Fayak, *Phys. B.* 291, 49 (2000).

[5] J.Smit and H.P.J.Wijn, Ferrites (Philips Tech. Library, 1959).

[6] RG Gupta and RG Mendiratta, *J. Appl. Phys.* 48, 845 (1977).

[7] J.M.Hastlings and L.M.Corliss, *Phys.Rev.* 104, 328 (1956).

[8] S. E. Harrison, W. S. Osmond, and P. W. Teale, *Phys. Rev.* 106, 865 (1957).

[9] Tahir Abbas, Y. Khan, Mushtaq Ahmad and Shahid Anwar, *Solid State Communications*, 82, 701 (1992).

[10] DH Lee, HS Kim, CH Yo, K Ahn, KH Kim, *Materials Chemistry and Physics* 57, 169 (1998).

[11] K. Krieble, T. Schaeffer, JA Paulsen, AP Ring, CCH Lo and JE Snyder, *J. Appl. Phys.* 97 10F101 (2005).

[12] O Caltun, GSN Rao, KH Rao, BP Rao, I. Dumitru , CO Kim and CG Kim, *J. Magn. Magn. Mater.*, 316, e 618 (2007).

[13] Sawazky, G.A., Van Der Woude, F., Morrish, A.H.: *Phys. Lett.* 25A (2), 147 (1967).

[14] Paulsen J A, Ring A P, Lo C C H, Synder J E and Jiles D C, *J.Appl.Phys.*97, 044502 (2005).

[15] Qiang-min wei, Jian-Biao Li, Yong-Jun Chen, *J.Mater.Sci.* 36, 5115 (2001).

[16] Qiangmin Wei, Jian-bao Li, Yong-jun Chen, Yong-sheng Han, *Mater Chem and Phys* 74, 340 (2002).

[17] Qiangmin Wei and Brian W.Robertson, *J. Solid State Chemistry* 176, 279 (2003).

[18] M. U. Rana, M. U. Islam and T. Abbas, *Mater. Lett.* 41, 52 (1999).

[19] K Srinivasa Rao, A Mahesh Kumar, M Chaitanya Varma, GSVRK Choudary, KH Rao *J. Alloys & Comp.,* 488,L6 (2010)

[20] RF Soohoo Theory and Applications of Ferrites, Vol.6, Englewood cliffs, Prentice Hall, NJ, 1960.

[21] AD Sheikh and VL Mathe *J. Mater. Sci.,* Vol.43, 2008, pp.2018.

[22] B Baruwati, RK Rana and SV Manorama, *J Appl. Phys.*, Vol.101, 2007, pp.014302

[23] V.K.Singh, N.K.Khatri and S.Lokanathan, *Pramana*, 16, 273 (1981).

[24] J Hu, H Qin, Y Wang, Z Wang, S Zhang, *Solid State Communications* 115, 233 (2000).

[25] E.W.Gorter, *Philips Res. Rep.* 9, 295 (1954).

[26] Uzma Ghazanfar, S.A.Siddiqi, G.Abbas, *Materials Science & Engineering B* 118, 84 (2005).