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PREPARATION OF $Ni_{1-x}Mn_xFe_2O_4$ FERRITES BY SOL-GEL METHOD AND STUDY OF CATION DISTRIBUTION

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Abstract

The nanoparticles of the spinel ferrite system $Ni_{1-x}Mn_xFe_2O_4$ with **x**=0.0, 0.1, 0.3, 0.5, 0.7 and 0.9 were prepared by sol-gel combustion technique using chlorides of Ni, Mn and Fe with citric acid as a source. The structure of ferrite materials and the particle size were determined by x-ray diffraction (XRD). It was observed that the structure is single phase, face centered cubic with lattice parameters and the particle size ranging from 8.365Å to 8.394Å and 23.86Å to 38.30Å respectively. The lattice parameter showed a linear dependence on concentration in accordance with the Vegard's law. By analyzing XRD patterns, the cation distribution over A and B-sites was estimated through R-Factor method. The magnetic moment for each sample was determined from cation distribution on the two sites. An enhancement in the net magnetic moment was observed with gradual increase in the Mn content.

Keywords: Cation distribution, Magnetic moments, Spinel ferrites, X-ray diffraction.

INTRODUCTION

Chemically prepared magnetic nanoparticles of system exhibit superior magnetic properties compared to their bulk counterparts due to small particle size and uniform distribution. Technically, spinel ferrites are an important group of materials with diverse properties applicable in the fabrication of electronic, magnetic and microwave devices. Nickel ferrites find applications in low as well as in high frequency devices due to high electrical resistivity, high mechanical hardness and good chemical stability. They are mostly used in magnetic recordings, telecommunication, power transformers, storage devices and drug delivery systems [Shobana *et al*. 2009].

The unit cell of the spinel ferrite is formed by doubling the face centered cubic oxygen sublattice along each of the three dimensions. In this arrangement 64 tetrahedral or A-sites and 32 octahedral or B-sites are created in the unit cell. In stoichiometric spinels only 8 A-sites and 16 B-sites are filled by divalent transition-metal ions. The spinel compounds belong to the space group Fd3m ($\mathbf{F}^{4}_{1/\mathbf{d}}\bar{3}_{2/\mathbf{m}}$, No. 227 in the International Tables for X-Ray Crystallography) with lattice parameter 8.5Å. In mixed spinel ferrites the concentrations of ferrous, ferric and substituted metal ions and their distribution over tetrahedral and octahedral sites play a vital role in determining their magnetic and electrical properties. In normal spinels, all the A-sites are occupied by divalent transition metal ions while in inverse spinels; the divalent ions occupy B-sites. In disordered spinels the divalent ions are present on both A and B-sites. The normal and inverse spinels are two extremes between which the cation distribution may vary. When the origin of the unit cell is taken at the centers of symmetry $\bar{4}3m$ and $\bar{3}m$, then oxygen positional parameter **u** (the distance between the oxygen ion and the face of the cube edge along the cube diagonal of the spinel subcell) has ideal values 0.375(3/8) and 0.250(1/4) respectively, for a perfect cubic close- packed arrangement of oxygen ions. In this case the octahedral cation-anion distance or bond length is 1.155 times larger than the tetrahedral bond length. A deviation from the ideal structure occurs when oxygen is displaced along [111] direction to accommodate the constituent cations, the tetrahedral site with smaller volume enlarges at the expense of the octahedral site and then **u** has a value greater than 0.375.

In order to control the domain of ferrites applications, the investigation of cation distribution on A and B-sites and oxygen positional parameter **u**, is most important [Abbas *et al*. 1992].

To determine the cation distribution in spinels many techniques have been employed so far, some of them are neutron diffraction [Stall *et al*. 1964], thermoelectric measurements [Wu and Mason 1981], electron spin resonance [Schmocker *et al*. 1978] etc. By analyzing the x-ray diffraction patterns cation distribution can be estimated by several methods, like Bertaut method [Rubio Gonzalez *et al*. 1985], Furuhashi method [Furuhashi *et al*. 1973], and R-Factor method [Rana *et al*. 1999].The investigations on the cation distribution for $NiFe_2O_4$ [Hugh *et al*. 1983], $NiMn_xFe_{2-x}O_4$ [Wei *et al*. 2001a], and $Ni_xMn_{1-x}Fe_2O_4$ [Wei *et al*. 2001b] have been reported. In the present work, R-Factor method has been employed to estimate the cation distribution and to calculate the oxygen positional parameter in $Ni_{1-x}Mn_xFe_2O_4$ ferrites.

EXPERIMENTAL

PREPARATION OF SAMPLES

The nanoparticle powders of $Ni_{1-x}Mn_xFe_2O_4$ with **x** = 0.0, 0.1, 0.3, 0.5, 0.7, and 0.9 were prepared by using sol-gel auto combustion method from reagent grade constituents, nickel chloride, manganese chloride and ferric chloride provided by Merck Germany. The ferrite powders were obtained through a procedure described below:

Sol-Formation

The stoichiometric amount of metal chlorides and citric acid was dissolved into de-ionized water to form a mixed solution. Homogenous distribution and segregation of the metal ions was achieved by the use of citric acid. The pH value of the solution was maintained in the range of 7 ~ 8 by drop wise addition of ammonia solution (base catalyst) in order to speed up the reaction. The solution was constantly stirred using a magnetic agitator. The condensation reaction took place between the adjoining metal chlorides and the molecules of citrates yielding a polymer precursor in colloidal dimensions known as sol.

Gel Formation

The obtained sol was heated at 80ºC on a hot plate under regular stirring to condensate into a xerogel.

Powder Formation

An increase of temperature upto 250ºC led to the ignition of the dry gel and a loose ferrite nanopowder was obtained through the burning of gel in a self-propagating combustion manner. During the combustion process, exothermic decomposition of a redox mixture of metal chlorides and citric acid took place along with the removal of gases such as Cl_2, CO, H_2O, and CO_2.

Annealing

The prepared powder samples were then annealed for 5 h at 500°C in order to enhance the crystallinity. These annealed powders were characterized by powder x-ray diffraction technique using an x-ray diffractometer Shimadzu XD-5A with Cu K-α source radiation of wavelength $\lambda = 1.5406$ Å, at room temperature. The phase constitution and structure of each composition were determined by indexing the XRD patterns.

SITE PREFERENCE ANALYSIS

R-Factor method was used to determine the values of the inversion parameter δ and oxygen positional parameter u in Ni-Mn ferrites. This method works well for the selection of the best fit simulated structure by minimizing the value of the residual function **R**. For this purpose a computer program in FORTRAN-77 was developed. The program was run for 10 to 100 iterations. The values of δ, **u** and **R** for each composition have been recorded to justify the site occupancies. Two of the several expressions used for the residual function **R** are as follows;

$$\mathbf{R}_1 = \frac{\sum_{\mathbf{hkl}} \left| \mathbf{I}_{\mathbf{obs}}^{\mathbf{hkl}} - \mathbf{I}_{\mathbf{cal}}^{\mathbf{hkl}} \right|}{\sum_{\mathbf{hkl}} \mathbf{I}_{\mathbf{obs}}^{\mathbf{hkl}}} \quad \textbf{(1)}$$

$$\mathbf{R}_2 = \frac{\sum_{\mathbf{hkl}} \left| \sqrt{\mathbf{I}_{\mathbf{obs}}^{\mathbf{hkl}}} - \sqrt{\mathbf{I}_{\mathbf{cal}}^{\mathbf{hkl}}} \right|}{\sum_{\mathbf{hkl}} \sqrt{\mathbf{I}_{\mathbf{obs}}^{\mathbf{hkl}}}} \quad \textbf{(2)}$$

Where $\mathbf{I}_{\mathbf{obs}}^{\mathbf{hkl}}$ and $\mathbf{I}_{\mathbf{cal}}^{\mathbf{hkl}}$ are the observed and calculated intensities for **hkl** reflection respectively. For the computation of the relative integrated intensity of a given diffraction line, the following formula is applicable.

$$I_{hkl} = |F|^2 PL_P \quad \textbf{(3)}$$

Where F is the structure factor, **P** is the multiplicity factor and **Lp** is the Lorentz-polarization factor.

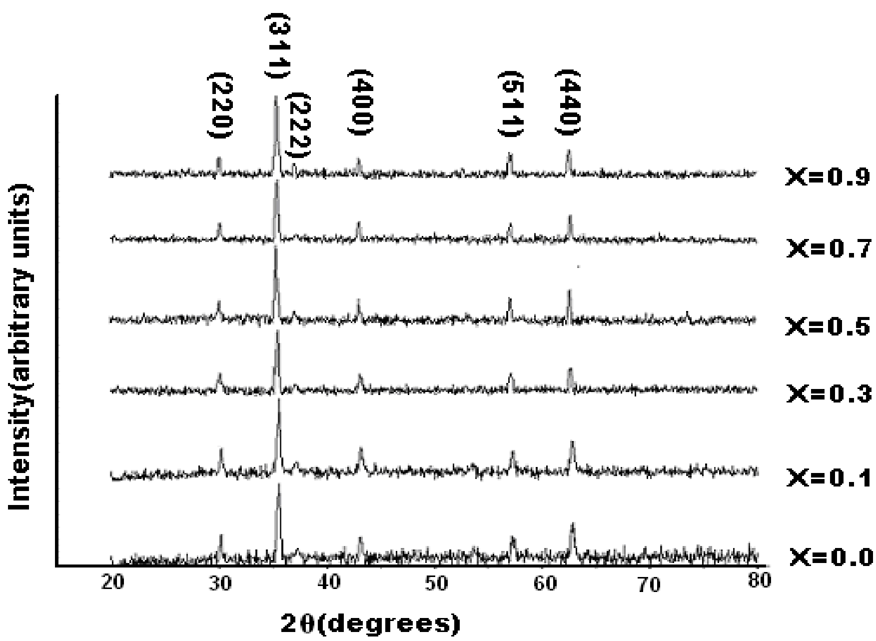

Fig. 1: X-ray diffraction patterns of $Ni_{1-x}Mn_xFe_2O_4$ system.

RESULTS AND DISCUSSION

PHASE ANALYSIS, PARTICLE SIZE OF FERRITE POWDERS

The diffraction lines in Fig. 1 provide a clear evidence of the formation of a pseudo solid solution of the $Ni_{1-x}Mn_xFe_2O_4$ ferrites. Mean value of the lattice parameter ***a***, calculated from six diffraction peaks of each sample shows a linear Mn content dependence shown in Fig. 2. Since the ionic radius of Mn^{2+} (Tet: 0.655 Å; Oct 0.80 Å) is greater than that of Ni^{2+} (Tet: 0.55Å; Oct: 0.69 Å) [Wei *et al.* 2001b], the replacement of nickel ion by manganese ion causes an increase in the interatomic spacing parameter ***d***' and consequently lattice parameter increases in accordance with Vegard's law [Cullity 1977]. The value of lattice parameter for the $NiFe_2O_4$ was found to be ***a*** = 8.365Å, which is in good agreement with that obtained from JCPDS card (10-0325), for nickel iron oxide, which is ***a*** = 8.339Å.

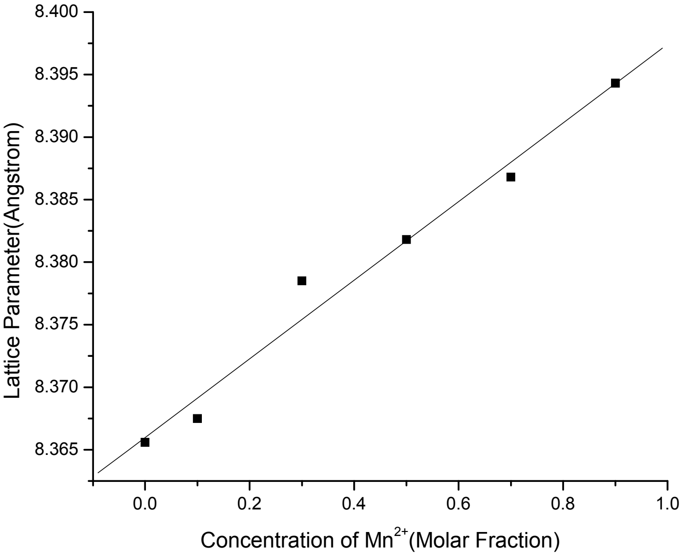

Fig. 2: Lattice parameter as a function of Mn content in $Ni_{1-x}Mn_xFe_2O_4$.

The particle size of the powders was determined by Scherer's equation [Attia 2006].

$$D_{hkl} = \frac{0.9\lambda}{B_{hkl}\cos\theta} \qquad \textbf{(4)}$$

Here $\mathbf{D_{hkl}}$ is the particle size obtained from the peak with maximum intensity which corresponds to Miller indices (311) in all XRD patterns. $\mathbf{B_{hkl}}$ is full width of the peak at half maximum (in radians). The particle size against each composition is shown in Table1.

Table 1: Particle size in $Ni_{1-x}Mn_xFe_2O_4$

Composition(**x**)	0.00	0.10	0.30	0.50	0.70	0.90
Particle size (nm)	3.86	6.47	0.33	31.64	33.85	38.30

The change in particle size is attributed to the ionic radii of the constituent metals [Zhong *et al.* 2006].The crystallites are more compact in the sample with **x** = 0.0, as Ni^{2+} ion is smaller one and can dissolve in the spinel lattice, substitution of Mn^{2+}ion causes increase in porosity of grains due to its greater ionic radius and the grains are no more compact causing an increase in particle size.

ESTIMATION OF CATION DISTRIBUTION

By inputting the data obtained from XRD patterns and fractional coordinates of lattice sites in a spinel cubic unit cell as listed in Table 2, the inversion parameters and oxygen positional parameters were calculated from the computer program by minimizing the value of residual function **R**.

Table 2: Fractional coordinates of lattice sites in a spinel cubic unit cell [Sickafus and Wills 1999].

Lattice sites	Equipoint	Point symmetry	Fractional coordinates of lattice sites
			Origin on $\bar{4}$3m at A-site cation (1/8,1/8,1/8 from $\bar{3}$m on octahedral vacancy) (0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0)+
A-site cation	8a	$\bar{4}$3m	0,0,0; 1/4,1/4,1/4
Tetrahedral vacancy	8b	$\bar{4}$3m	1/2,1/2,1/2; 3/4,3/4,3/4
B-site cation	16d	$\bar{3}$m	5/8,5/8,5/8; 5/8,7/8,7/8;7/8,5/8,7/8; 7/8,7/8,5/8
Octahedral vacancy	16c	$\bar{3}$m	1/8,1/8,1/8; 1/8,3/8,3/8;3/8,1/8,3/8; 3/8,3/8,1/8
Anion	32e	3m	u,u,u; u, $\bar{u}$, $\bar{u}$; $\bar{u}$,u, $\bar{u}$; $\bar{u}$, $\bar{u}$,u;(1/4 –u),(1/4 –u),(1/4 –u);(1/4 +u),(1/4 +u),(1/4 –u);(1/4 +u),(1/4 –u),(1/4 +u);(1/4 –u),(1/4 +u),(1/4 +u)
Tetrahedral vacancy	48f	mm	1/4,0,0; 0,1/4,0;0,0,-1/4; -1/4,0,0;0,-1/4,0; 0,0,-1/4;1/2,1/4,1/4; 1/4,1/2,1/4;1/4,1/4,1/2; 0,1/4,1/4;1/4,1/4,0; 1/4,0,1/4

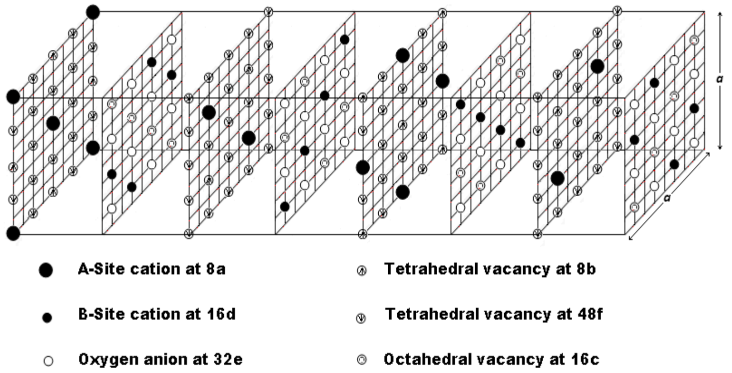

Fig. 3: Spinel lattice sites in a cubic cell, layers are shown at ***a/8*** interval along [100] cubic cell axis.

The general formula used for cation distribution in $Ni_{1-x}Mn_xFe_2O_4$ ferrites is expressed as;

$$\mathbf{Me}^{\mathbf{3+}}_{\mathbf{1\text{-}\delta}}\boldsymbol{Me}^{2+}_{\delta}[\boldsymbol{Me}^{3+}_{1+\delta}\boldsymbol{Me}^{2+}_{1-\delta}]\boldsymbol{O}_4 \tag{5}$$

The brackets are used to represent the cations at octahedral sites, δ represents the inversion parameter. Inversion parameter δ, oxygen positional parameter **u** and residual function **R** for $Ni_{1-x}Mn_xFe_2O_4$ are listed in Table 3. The cation distribution for $Ni_{1-x}Mn_xFe_2O_4$ is listed in Table 4.

Table 3: Inversion parameter δ, Oxygen positional parameter **u** and Residual function **R** for $Ni_{1-x}Mn_xFe_2O_4$.

x	δ	**u**	**R**
0.0	0.1	0.377	0.064
0.1	0.1	0.378	0.066
0.3	0.2	0.380	0.071
0.5	0.3	0.380	0.065
0.7	0.4	0.381	0.082
0.9	0.5	0.381	0.056

Table 4: Cation distribution in $Ni_{1-x}Mn_xFe_2O_4$

Concentration(x)	Distribution of cations					
	Tetrahedral site(A)			Octahedral site(B)		
	Ni^{2+}	Mn^{2+}	Fe^{3+}	Ni^{2+}	Mn^{2+}	Fe^{3+}
0.0	0.1	0.0	0.9	0.9	0.0	1.1
0.1	0.09	0.01	0.9	0.81	0.09	1.1
0.3	0.14	0.06	0.8	0.56	0.24	1.2
0.5	0.15	0.15	0.7	0.35	0.35	1.3
0.7	0.12	0.28	0.6	0.18	0.42	1.4
0.9	0.05	0.45	0.5	0.05	0.45	1.5

According to our results a gradual increase in inversion parameter with **x** implies that nickel ferrite is an inverse spinel and manganese ferrite is a normal one. It is deduced that lattice parameter and oxygen positional parameter are directly related to the degree of inversion.

CALCULATION OF MAGNETIC MOMENT

The magnetic moments of A-site cations and B-site cations oppose each other in an applied magnetic field [Smith 1990]. The ionic magnetic moments for ions of 3d transition elements Fe^{3+}, $Ni^{2+}$and $Mn^{2+}$are $5\mu_B$, $2\mu_B$ and 5 μ_B respectively [Smith 1990]. The distribution of cations on the two sites in spinels determines the net magnetic moment of the formula unit. In the present work, by the induction of Mn^{2+} ions in $Ni_{1-x}Mn_xFe_2O_4$ ferrites, Fe^{3+}ions start migrating from A-site to B-site causing more imbalances in spins between the two sites, consequently the magnetization at B-site (M_B) is increased; and A-B interaction gives the net magnetic moment, as shown in Table 5.

Table 5: Magnetic moment for $Ni_{1-x}Mn_xFe_2O_4$

Concentration(**x**)	0.0	0.1	0.3	0.5	0.7	0.9
Magnetic moment(μ_B)	2.60	2.84	3.74	4.40	4.82	5.00

CONCLUSIONS

The $Ni_{1-x}Mn_xFe_2O_4$ nanoparticles can be prepared using sol-gel technique. The phase identification and estimation of cation distribution is possible to carry out on the basis of XRD data. The values of inversion parameter and oxygen positional parameter show that the ferrites system belongs to a family of mixed or partially inverse spinels. It was observed that particle size in the ferrites tended to increase as the degree of inversion increased. The relationship among structural parameters (***a***, **u**) and the inversion parameter (δ) was studied, it was found that the lattice parameter was dependent on the average effective cation radius in the compound and had no significant dependence on the arrangement of cations; however the oxygen parameter was dependent on the distribution of cations.

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