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X-ray Diffraction and Site Preference Analysis of Ni-Substituted $MgFe_2O_4$ Ferrites

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Abstract: A series of $Mg_{1-x}Ni_xFe_2O_4$ spinel ferrites with x = 0.0, 0.25, 0.50, 0.75 and 1.0 have been prepared using standard ceramic method. The relationship between structural parameters and concentration of the substituted Ni-ions has been studied. A determination of crystal structure, oxygen positional parameter and cation distribution using X-ray Diffraction (XRD) and R-factor method revealed that these ferrites belong to the family of mixed or partially inverse spinels.

Key Words: Ferrites, Diffraction, Cation Distribution

Introduction

Structure factor simulation of ferrites is important because the crystallographic, magnetic, and electrical properties and even the perfection of heat treatment is the function of cation distribution amongest the A- and B-sites Rana *et al.*, 1999; Uitert, 1956; Naik and Power, 1985; Smit and Wijn 1959. It has been well established that if the lattice constant varies linearly with the composition it follows Vegard's law. It is a good tool to predict about the distribution of the cations on A- and B-sites. Positive deviations from Vegard's law occurs when the tendency for complete solid solution is small or when the solid solution pattern of order is destroyed. Negative deviations occurs when some ion occurs at different crystallographic positions with different chemical bond or when in the solid solution pattern of order persists. It is reported that the lattice constant depends linearly on the chemical composition of spinel ferrites like Ni-Ge ferrites, Cd-Zn ferrites, gallium substituted magnesium ferrite, Mn-Sn ferrites, Ni-Zn ferrite, Mn-Zn ferrite, Cu-Zn ferrite and Calcium substituted cobalt ferrites Romejin, 1953; Arean *et al.*, 1990; Romeijn, 1953; Yamada, 1990; Srinivasan *et al.*, 1988; Murthy *et al.*, 1969; Abbas *et al.*, 1992; Kulkarni and Patil, 1982 and Baldha *et al.*, 1989. The cation distribution and oxygen positional parameter have been found Gonzalez and Arean, 1985; Gorter, 1954; Blasse, 1964; Khan and Kneller, 1978; Verwey *et al.*, 1947 and Rana *et al.*, 2000 using different calculation procedures both for binary and ternary spinels, from X-ray diffraction data. The Bertuat, Furuhashi, and R-factor methods were used to study the cation distribution of $CuGa_2O_4$, $Cd_{0.75}Fe_2O_4$ and $Cu_{0.6}Zn_{0.4}Al_2O_4$ ferrites prepared by solid state reaction technique Gonzalez and Arean, (1985) and were critically analyzed and compared to get reliable results. R-factor method has been used for the determination of cation distribution in gallium substituted cobalt ferrites Arean, (1990). By means of detailed X-ray diffraction study of a large number of oxides having spinel structure like $MgCr_2O_4$, $NiCr_2O_4$, $CuCr_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, $Cu_xZn_{1-x}Fe_2O_4$, $CdFe_2O_4$, $TiZn_2O_4$, $SnZnO_4$, $SnCo_2O_4$, $Fe^{2+}Fe^{3+}A_{l2}O_4$, $LiA_{1.5}O_5$ Verwey, (1947) and a large number of solid solution containing these and other spinel, have been studied whether they crystallize in the "normal" spinel structure $A_xY_2O_4$ or in the "inverse" type of structure $Y(XY)O_4$ discovered by Barth and Posnjak, 1932; Gorter, (1954); Srivastava *et al.*, (1987). In the present work R- factor has been employed on tetrahedral
(A-sites) and octahedral (B-sites) in Ni-substituted $MgFe_2O_4$ ferrites.

Experimental

Preparation of Samples: The $Mg_{1-x}Ni_xFe_2O_4$ ferrites of different compositions were prepared using ceramic technique involving solid state reaction from metal oxides ($MgCo_3$, NiO and Fe_2O_4) in the form of grained powder having 99.99% purity supplied by Emerk, Germany. The qualitative compositions of each sample were calculated in terms of weight percentage according to the following chemical reaction:

$$MgCO_3(1-x) + NiO(x) + Fe_2O_3 \rightarrow Mg_{1-x}Ni_xFe_2O_4 + (1-x)CO_2 \uparrow$$

The required weight percentage of oxide materials were ground to fine powder (particle size <50 μm) in an agate mortar and the grinding continued for about an hour till a homogeneous mixture was obtained. The finally ground powder was cold pressed under the load of 30 kN using hydraulic press. To promote crystallization heat treatment was carried out in steps. To avoid surface damaging and bubbling the pallets were put in a preheated tube furnace at 400 ^oC. Then the furnace temperature was increased gradually upto 1000 ^oC with a step of 100 ^oC. The samples were heat treated at 1000 ^oC for 45 hrs. For the completion of reaction final sintering was carried out at 1200 ^oC for 5 hrs. Then the samples were quenched in air to obtain the equilibrium of cations distribution.

A Shimadzu XD-5A diffractometer equipped with Cu-Kα radiation source, was employed to identify the phase constitution and structure of air cooled pellets. For phase identification each sample was scanned from 2θ=20-65 degrees. The XRD patterns were analysed to calculate d-values (interatomic spacing) and hkl's. The relative intensities were taken from XRD pattern, using highest peak as reference, for cation distribution purposes.

Site Preference Analysis: To determine cation distribution and oxygen position parameter, u, in $Mg_{1-x}Ni_xFe_2O_4$ ferrites R-Factor method is used, since in this method the best structure is selected so as to minimize the value of a residual function R. A computer program in FORTRAN-77 based on R-factor was developed for this purpose.

The program was run for 10 to 100 iterations until the minimum value of the residual function R is obtained. The inversion parameter, oxygen positional parameter and residual factor for each concentration of MgNi ferrite have been calculated. Several expressions for the residual function, R are proposed, two of these are:

$$R_1 = \frac{\sum_{hkl} |I_{obs}^{hkl} - I_{cal}^{hkl}|}{\sum I_{obs}^{hkl}} \quad \text{and}$$

$$R_2 = \frac{\sum_{hkl} |\sqrt{I_{obs}^{hkl}} - \sqrt{I_{cal}^{hkl}}|}{\sum_{hkl} \sqrt{I_{obs}^{hkl}}}$$

where I_{obs}^{hkl} and I_{cal}^{hkl} are observed and calculated intensities for hkl reflections.

Results and Discussion

X-Ray Diffraction Analysis: The XRD patterns of $Mg_{1-x}Ni_xFe_2O_4$ system for all the compositions (x = 0.0, 0.25, 0.50, 0.75 and 1.0) are shown in Fig. 1. The analysis of the results of the diffraction patterns gave a verification of the presence of spinel structure for each composition in $Mg_{1-x}Ni_xFe_2O_4$ system. The hkl, xx and d- values of each composition of Ni substituted Mg ferrites are listed in Table 1. The d-spacing were compared by the JCPDS tables Bayliss *et al.*, (1996) for spinel structure.

Lattice Parameters: The lattice constant as a function of the concentration of the Ni in Mg-Ni ferrites are depicted in Fig. 2. The decreasing trend in the lattice constant (i.e. from 8.432 Å to 8.368Å) with increasing concentration of Ni is observed. Although the ionic radii of the Mg and Ni are nearly equal but by replacing Mg by Ni, the lattice constant decreases because of the simultaneous influence of the radius effect and the energy level effect Arean, 1990; Romeijn, 1953. On substitution of Ni, redistribution of charges which is decreasing on the average and also taking into consideration the influence of electric field of the surrounding oxygen ions upon electrons, the lattice will shrink. The apparent radius will decrease, which results in the decrease in the lattice constant. The average change in the lattice constant in going from $MgFe_2O_4$ to $NiFe_2O_4$ again lies between the inverse and normal spinel leading to the fact that $Mg_{1-x}Ni_xFe_2O_4$ belong to family of mixed or partially inverse spinels.

Cation Distribution: The values of the inversion parameter, oxygen positional parameter and residual function for $Mg_{1-x}Ni_xFe_2O_4$ ferrite family by varying the concentration of Ni by x = 0.0, 0.25, 0.50, 0.75 and 1.0 were calculated by inputting XRD data obtained from diffraction patterns. The results are listed in Table 2. The site preference of cations on tetra, and octahedral sites is presented in Table 3. The general formula of cation distribution for a mixed ferrite is given by:

$$[Me^{2+}_{\delta}\ Fe_{1-\delta}]_A\ [Me^{2+}_{1-\delta}\ Fe^{3+}_{1+\delta}]_B O_4$$

Where Me^{2+} stand for metal ions which in our case are Mg^{2+} and Ni^{2+}. Results of the Table 3, indicate that both Mg^{2+} and Ni^{2+} ions have the preference for octahedral B-site, hence it is suggested that MgNi-ferrites belong to the family of mixed spinels (i.e., partially inverse). The cation-anion and cation-cation distances are calculated using the experimental values of lattice constant and oxygen positional parameter and are presented in Tables 4 and 5 using the following equations Rana *et al.*, 1999 and Abbas *et al.*, 1992.

$$d_{AX} = a\sqrt{3}\left(u - \frac{1}{4}\right)$$

$$d_{AX} = a\left(3u^2 - \frac{11}{4u} + \frac{43}{64}\right)^{\frac{1}{2}}$$

$$d_{xx} = a\sqrt{2}\left(2u - \frac{1}{2}\right)$$

$$d_{xx} = a\sqrt{2}(1 - 2u)$$

$$d_{xx} = a\left(4u^2 - 3u + \frac{11}{16}\right)^{\frac{1}{2}}$$

The results of the Table 3, show the site preference of Mg^{2+} and Ni^{2+} ions on the tetrahedral and octahedral sites. Since Mg and Ni ions both prefer octahedral site, and only a small portion of these ions occupy the tetrahedral site, which is supported by a low value of $\delta = 0.1$, which remains constant with the substitution of Ni in $Mg_{1-x}Ni_xFe_2O_4$ ferrites. The oxygen positional parameter have the values ~ 0.324 for all the concentrations except for x =0.08, 0.25 for which u= 0.325. Our low values of δ and the u-values calculated for this family are less then 0.375, where the origin is taken at one of the octahedral sites may be due to the irregularities in the crystal structure which appear in the calculation of lattice constant, the distribution of cations among the tetrahedral and octahedral sites and the partially inverse spinel structure in Mg-ferrites, are in good agreement with the results reported earlier Romejin, 1953; Gorter, 1954; Blasse, 1964; Sagar, 1988 and Krezhov and Konstantinov, 1992.

Conclusion

The distribution of cations on tetrahedral (A) and octahedral (B) sites in $Mg_{1-x}Ni_xFe_2O_4$ ferrite system using XRD and R-factor method has revealed that the Ni substituted Mg-ferrites belong to the family of mixed or partially inverse spinel.

Table 1: XRD Parameters of MgNi Ferrites

Sr. No.	x = 0.0		x = 0.25		x = 0.50		x = 0.75		x = 1.0	
	hkl	d(Å)	hkl	d(Å)	hkl	d(Å)	hkl	d(Å)	hkl	d(Å)
1	220	3.01	220	2.99	220	2.98	220	2.97	220	2.96
2	311	2.56	311	2.55	311	2.53	311	2.53	311	2.52
3	400	2.13	400	2.11	400	2.10	400	2.10	400	2.09
4	333	1.65	333	1.62	333	1.60	333	1.61	333	1.61
5	440	1.47	440	1.47	400	1.48	400	1.48	400	1.48

Table 2: Inversion Parameter (δ), Oxygen Positional Parameter (μ) and Residual Factor (R) for $Mg_{1-x}Ni_xFe_2O_4$ Ferrite

Concentration (x)	δ	U	R
0.0	0.1	0.325	0.01
0.25	0.1	0.325	0.09
0.50	0.1	0.324	0.09
0.75	0.1	0.324	0.08
1.00	0.1	0.324	0.15

Table 3: Cation Distribution in $Mg_{1-x}Ni_xFe_2O_4$ Ferrites

Concentration (x)	Cation distribution					
	Tetrahedral site (A)			Octahedral site (B)		
	Mg^{2+}	Ni^{2+}	Fe^{3+}	Mg^{2+}	Ni^{2+}	Fe^{3+}
0.0	0.100	0.0	0.9	0.9	0.0	1.1
0.25	0.075	0.025	0.9	0.675	0.225	1.1
0.50	0.05	0.05	0.9	0.45	0.45	1.1
0.75	0.025	0.075	0.9	0.225	0.675	1.1
1.0	0.0	0.1	0.9	0.0	0.9	1.1

Table 4: Cation-Anion Distance in MgNi Ferrites

Mole fraction (x)	Distance Me-O			
	p(Å)	q (Å)	r(Å)	s (Å)
0.0	2.54	1.094	37.092	3.501
0.25	2.53	1.095	37.054	3.408
0.50	2.52	1.091	36.927	3.396
0.75	2.52	1.094	36.830	3.385
1.0	2.52	1.092	36.745	3.377

Table 5: Cation-Cation Distance in MgNi-Ferrites

Mole fraction (x)	Distance Me-Me				
	b(Å)	c(Å)	d(Å)	e(Å)	f(Å)
0.00	2.992	3.498	3.675	5.487	5.171
0.25	2.981	3.495	3.651	5.477	5.163
0.50	2.970	3.484	3.638	5.458	5.146
0.75	2.965	3.477	3.632	5.447	5.136
1.00	2.958	3.469	3.623	5.435	5.124

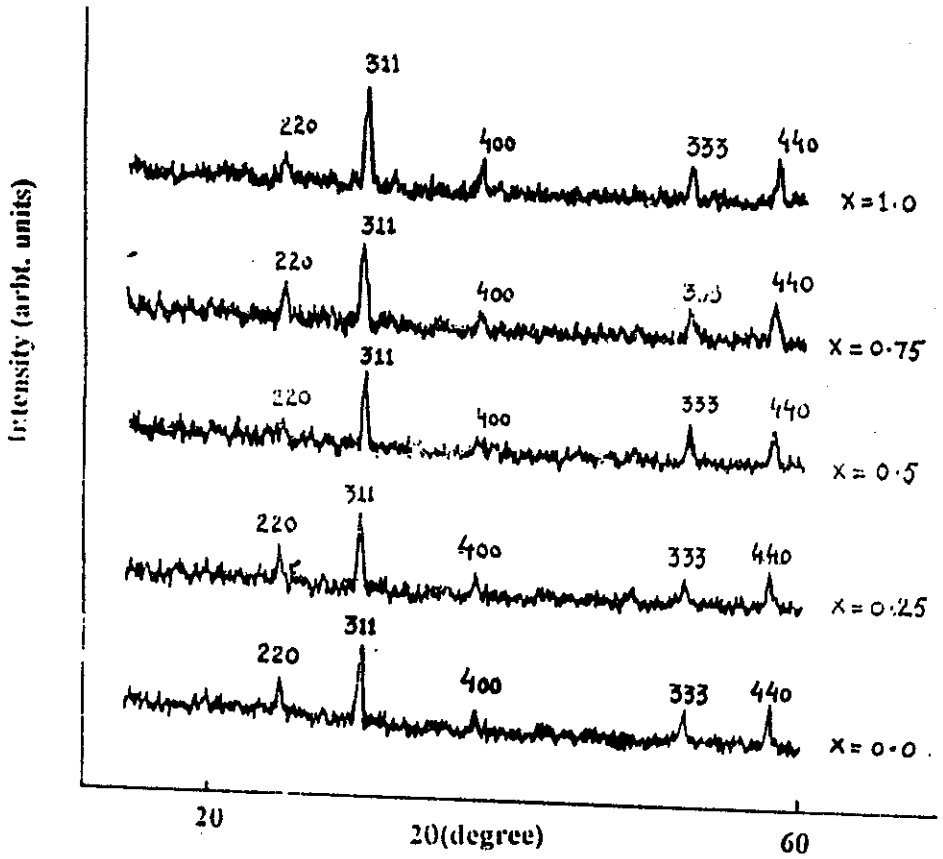

Fig. 1: XRD Patterns of $Mg_{1-x}Ni_xFe_2O_4$ Ferrites for Different Ni Composition

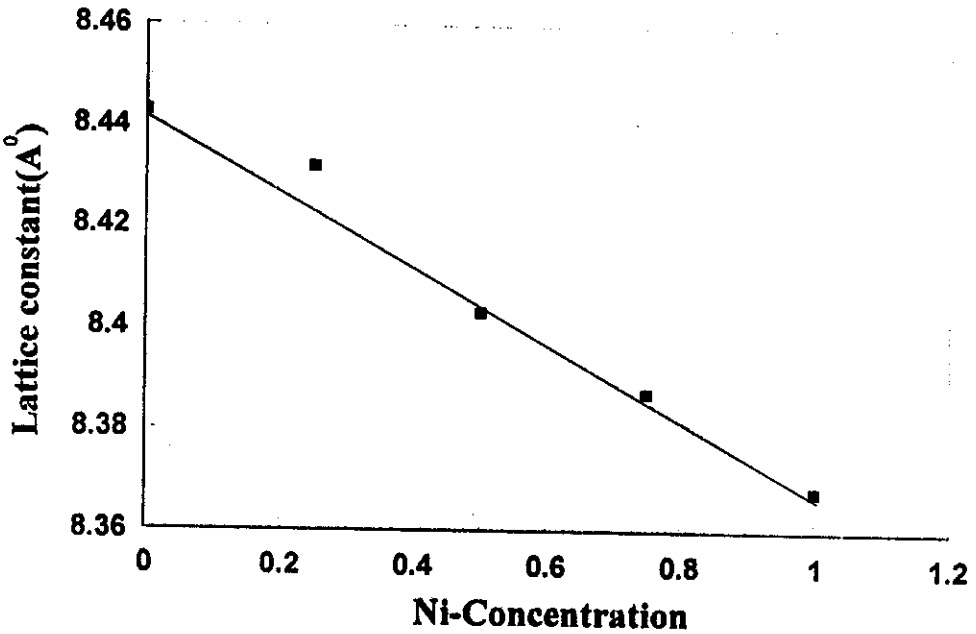

Fig. 2: Lattice Constant Versus Ni-Concentration in $Mg_{1-x}Ni_xFe_2O_4$ Ferrites

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