

1-1-2001

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LADGAONKAR, B. P.; VASAMBEKAR, P. N.; and VAINGANKAR, A. S. (2001) "Cation Distribution and Magnetisation Study of Nd⁺³ Substituted Zn-Mg Ferrites," *Turkish Journal of Physics*: Vol. 25: No. 2, Article 7. Available at: <https://journals.tubitak.gov.tr/physics/vol25/iss2/7>

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Cation Distribution and Magnetisation Study of Nd³⁺ Substituted Zn-Mg Ferrites

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Received 27.01.1999

Abstract

Polycrystalline ferrites $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ ($x = 0.00, 0.20, 0.40, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) were prepared by standard ceramic method. The compositions, on characterisation by X-ray diffraction, shows formation of single phase cubic spinels. Magnetic measurement of these composition shows increase in magnetic moment n_β with Zn^{2+} concentration up to $x = 0.4$ and decreases thereafter. This is attributed to the existence of localised canted spin. The compositions for $x = 0.8$ and 1.0 shows paramagnetic behaviour at and above room temperature. The trivalent substitution of Nd^{3+} ion causes reduction in the magnetic moment. The cation distribution of the system was investigated by comparing observed and calculated Curie temperatures, employing a modified Upadhyay model, wherein relative weighted magnetic interaction per formula unit is considered. From this it is found that the Zinc shows strong occupancy on tetrahedral sites, whereas magnesium ion preferentially distributes among A and B sites, showing maximum occupancy on A sites for $x = 0.20$. The substitution of Nd^{3+} ion causes an increase in the occupancy of magnesium ion on A sites.

Key Words: Polycrystalline Ferrite; Cation distribution; Magnetisation; Weighted interaction; Curie Temperature.

Introduction

Ferrimagnetic oxide, ferrite, crystallizes with two magnetic sub-lattices, tetrahedral (A) site and octahedral (B) site. The electrical and magnetic properties upon which its application depends, depend on the distribution of cations among these sites. The cation distribution may obtained from structural investigation [1]. For investigation of cation distribution Gilleo's statistical model [2, 3], which assumes three magnetic ions per formula unit, can be employed. Systems such as Mg-Cd, Cu-Cd, Mg-zn, Ni-Cd-ferrites do not have three magnetic ions per formula unit. Therefore for such systems the modified

Upadhyay et al model [4, 5], which assumes relative weighted magnetic interaction per formula, unit can be used. The cation distribution in Zn^{2+} , Cd^{2+} and Mg^{2+} containing ferrites have been reported [1, 6, 7]. But reports on cation distribution in rare-earth substituted Zn-Mg-ferrite found to be rare. In the present communication, the results of estimation of cation distribution, employing a modified Upadhyay model for Nd^{3+} substituted Zn-Mg ferrite system are reported.

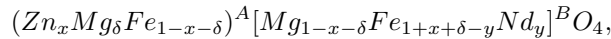
Experimental

Compositions of $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ ($x = 0.00, 0.20, 0.40, 0.60, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) polycrystalline ferrites were prepared by standard ceramic technique, by using AR grade oxides ZnO , MgO , Fe_2O_3 and Nd_2O_3 , wherein double sintering is employed. The sintering temperature was maintained at $1000^\circ C$ for 24 hours and then furnace cooled, at the rate of $80^\circ C$ per hour, to the room temperature. Characterisation of the compositions were performed by X-ray powder diffraction on a Philips computerised x-ray diffractometer PW 1710 using $CuK\alpha$ radiation. The magnetisation measurement was carried out using a high field loop tracer. The measurement of Curie temperatures were done according to the Lorria-Sinha method [9].

Results and Discussion

X-ray diffractograms of the compositions reveal formation of single phase, cubic spinel ferrites, showing no ambiguous reflections. Typical X-ray diffraction diagrams for the compositions $x = 0.60$; $y = 0.00, 0.05$ and 0.10 are depicted in figure 1 to 3. The lattice constant a is calculated for different compositions and plotted against Zn^{2+} concentration, as presented in Figure 4. The lattice parameter shows increasing trend with Zn^{2+} concentration obeying Vegard's law. This can be attributed to large ionic radius of Zn^{2+} ion ($R_{Zn^{2+}} = 0.83 \text{ \AA}$) [8], which when substituted in the lattice resides on tetrahedral (A) sites and displaces smaller Fe^{3+} ion ($R_{Fe^{3+}} = 0.67 \text{ \AA}$) [8] from A sites to B sites. This suggests the strong occupancy of Zn^{2+} ion on A sites.

Magnetisation data for the composition is presented in Table 1. The magnetic moment, $n\beta$, as in Table 1, is shown increasing with Zn^{2+} concentration, showing a peak value at $x = 0.40$ and then decreases thereafter. The composition for $x = 0.80$ and 0.10 show paramagnetic behaviour at and above room temperature. similar results were reported for Zn-Mg ferrites [10, 11]. The substitution of Nd^{3+} ion in the lattice of Zn-Mg ferrites results into reduction in saturation magnetisation and magnetic moment. This reduction in magnetic moment may be due to room temperature magnetic moment ($3.3 \mu_B$) of Nd^{3+} ion, residing on octahedral B-sites and results into dilution magnetisation on B-sites, which suggests occupancy of Nd^{3+} ion on B-sites. Magnesium ions show preferential distribution among A and B sites [12]. The formula used to propose the cation distribution is,



where δ is ε distribution parameter, and gives the amount of Mg^{2+} ion occupying A-sites.

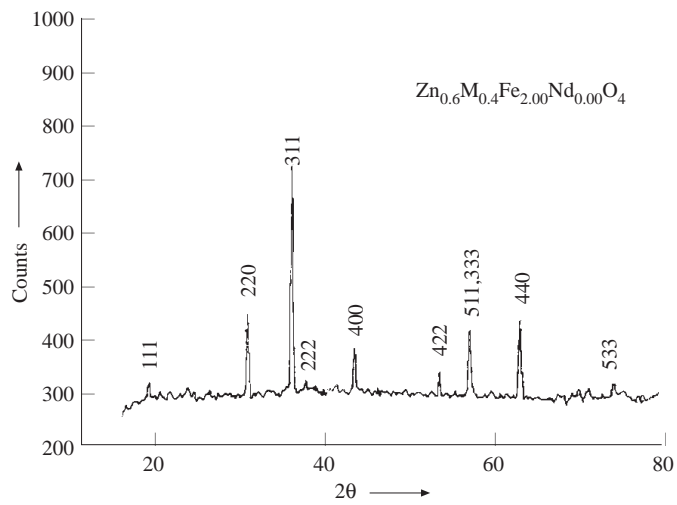


Figure 1. X-ray diffraction pattern of $\text{Zn}_x\text{Mg}_{1-x}\text{Fe}_{2-y}\text{Nd}_y\text{O}_4$ system for $x = 0.6$; $y = 0.00$

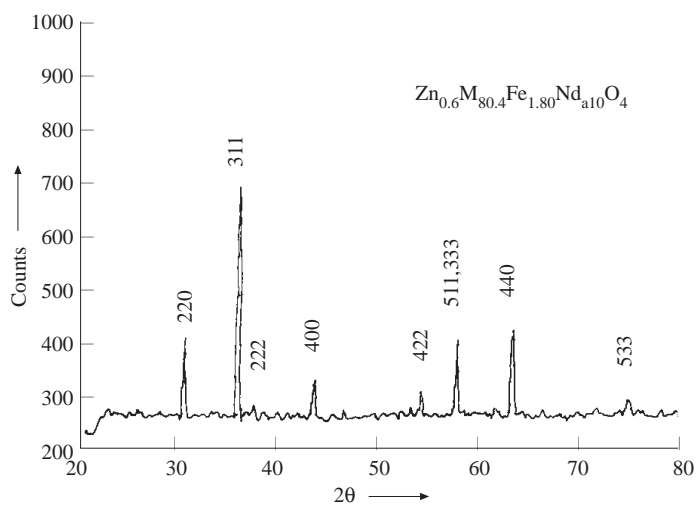


Figure 2. X-ray diffraction pattern of $\text{Zn}_x\text{Mg}_{1-x}\text{Fe}_{2-y}\text{Nd}_y\text{O}_4$ system for $x = 0.6$; $y = 0.05$

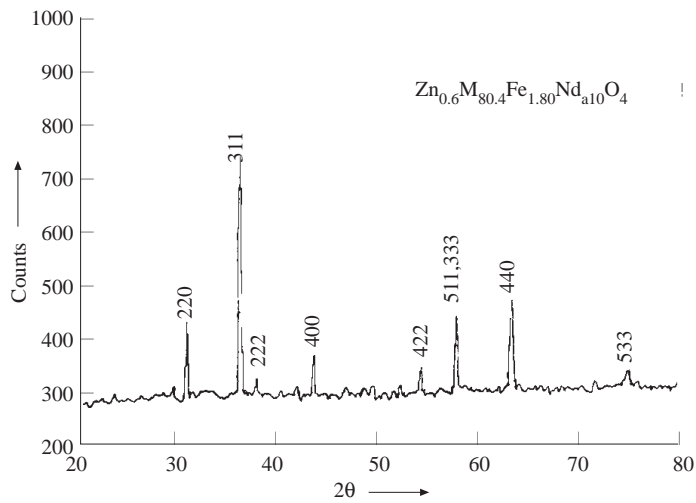


Figure 3. X-ray diffraction pattern of $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ system for $x = 0.6$; $y = 0.10$

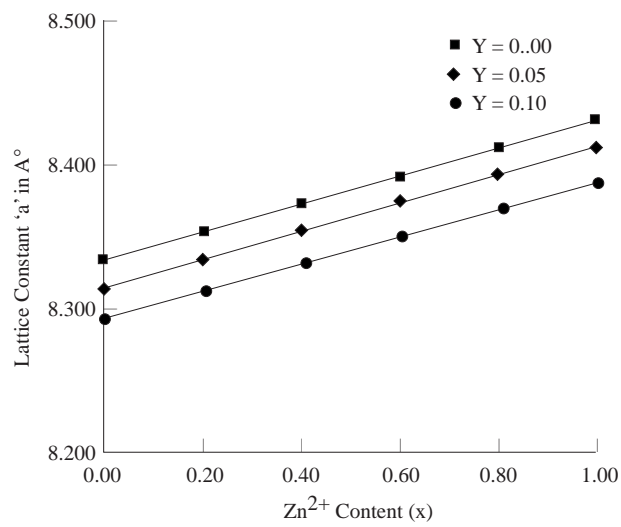


Figure 4. Variation of Lattice constant 'a' in Å against Zn^{2+} (x) content for $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$.

Table 1. Magnetisation data for the composition $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$.

x	Saturation Magnetisation			Magnetic Moment		
	'M _s ' in emu/gm			'n _β ' in μ _B		
	y = 0.00	y = 0.05	y = 0.10	y = 0.00	y = 0.05	y = 0.10
0.00	29.565	25.350	21.171	1.06	0.927	0.794
0.20	32.289	30.780	28.560	1.21	1.170	1.107
0.40	54.461	48.678	44.093	2.11	1.923	1.775
0.60	12.800	8.746	5.333	0.515	0.358	0.223
0.80	-	-	-	-	-	-
1.00	-	-	-	-	-	-

Gellio's statistical model can be used to investigate cation distribution, which assumes three magnetic ions per formula unit [2, 3]. The present system does not consist of three magnetic ions; hence the modified Upadhyay model [4, 5], which is based on relative weighted magnetic interaction per formula unit, is used for investigation of cation distribution. According to this model the Curie temperature is given by,

$$T_c(x) = \frac{M^*(x=0.00)n(x)}{M^*(x)n(0.00)}T_c(x=0) \quad (1)$$

$$M^*(x) = 2 + (1-x)\mu'_M/\mu_{Fe} \quad (2)$$

$$n(x) = 24/\mu_{Fe}^2[z\delta\mu_M'^2 + (\delta w + z^2)\mu'_M\mu_{Fe} + wz\mu_{Fe}^2] \quad (3)$$

$$z = 1 - x - \delta \text{ and } w = 1 + x + \delta.$$

where, $T_c(x=0.00)$ is Curie temperature at $x=0.00$, μ'_M and μ_{Fe} are magnetic moment of Mg^{2+} ion ($n\beta = 0 \mu_B$) and Fe^{3+} ion ($n\beta = 5\mu_B$, respectively, and x is the Zn^{2+} concentration. $n(x)$ is relative weighted magnetic interaction per formula unit. The above model has been modified for trivalent substitution [5] in order for investigation of cation distribution in Nd^{3+} substituted ferrites. Accordingly the relation for $M^*(x)$ is modified to,

$$M^*(x) = (2-y) + (1-x)\frac{\mu'_M}{\mu_{Fe}} + y\frac{\mu''_M}{\mu_{Fe}}, \quad (4)$$

where μ''_M is the magnetic moment of Nd^{3+} ion ($3.3\mu_B$ [15]) and y is concentration of Nd^{3+} ion. The relation for weighted magnetic interaction $n(x)$ is modified to,

$$n(x) = 24/\mu_{Fe}^2[z\delta\mu_M'^2 + (\delta w + z^2)\mu'_M\mu_{Fe} + wz\mu_{Fe}^2 + \delta y\mu'_M\mu''_M + zy\mu_{Fe}\mu''_M], \quad (5)$$

$$w = 1+x+\delta-y.$$

The Curie temperatures are calculated by from (1), by varying the distribution parameter δ from 0 to 1-x. The exact value of δ is decided, where the calculated Curie temperature and experimentally observed ones show good agreement. The calculated and observed temperatures along with cation distribution are presented in Table 2. On inspection of Table 2, it can be found that Zn^{2+} ion show strong occupancy on tetrahedral (A) sites, whereas Mg^{2+} ion show partial distribution among A and B sites. The inversion of Mg^{2+} ion, for composition $x=0.00$ and $y = 0.0$ found to be 87.6%, showing only 0.122 of magnesium on A sites. The occupancy of Mg^{2+} ion on tetrahedral (A) sites δ increases with Zinc concentration up to $x = 0.20$ and thereafter decreases. The cation distribution for MgFe_2O_4 ferrite shows good agreement with the previous reports [6, 12]. As depicted in Table 2, the Curie temperatures shows decreasing trend with zinc concentration. This may be due to zinc, which sits on A sites and decreases the strength of inter interaction J_{AB} .

Table 2. Cation Distribution and Curie Temperature Data for the Compositions $\text{Zn}_x\text{Mg}_{1-x}\text{Fe}_{2-y}\text{Nd}_y\text{O}_4$.

Zn ²⁺ Conc. x	Nd ³⁺ Conc. y	Cation Distribution	Curie Temperature T _c in K	
			Observed From Expt.	Calculated by Eq. (1)
0.00	0.00	(Zn _{0.00} Mg _{0.122} Fe _{0.878}) ^A [Mg _{0.878} Fe _{1.122} Nd _{0.00}] ^B O ₄	675	675
0.20	0.00	(Zn _{0.20} Mg _{0.186} Fe _{0.614}) ^A [Mg _{0.614} Fe _{1.386} Nd _{0.00}] ^B O ₄	558	560
0.40	0.00	(Zn _{0.40} Mg _{0.178} Fe _{0.442}) ^A [Mg _{0.422} Fe _{1.578} Nd _{0.00}] ^B O ₄	455	456
0.60	0.00	(Zn _{0.60} Mg _{0.064} Fe _{0.336}) ^A [Mg _{0.336} Fe _{1.644} Nd _{0.00}] ^B O ₄	383	383
0.80	0.00	(Zn _{0.80} Mg _{0.000} Fe _{0.200}) ^A [Mg _{0.200} Fe _{1.800} Nd _{0.00}] ^B O ₄	-	-
1.00	0.00	(Zn _{1.00} Mg _{0.000} Fe _{0.000}) ^A [Mg _{0.000} Fe _{2.000} Nd _{0.00}] ^B O ₄	-	-
0.00	0.05	(Zn _{0.00} Mg _{0.124} Fe _{0.876}) ^A [Mg _{0.876} Fe _{1.074} Nd _{0.05}] ^B O ₄	640	638
0.20	0.05	(Zn _{0.20} Mg _{0.217} Fe _{0.583}) ^A [Mg _{0.583} Fe _{1.367} Nd _{0.05}] ^B O ₄	512	516
0.40	0.05	(Zn _{0.40} Mg _{0.208} Fe _{0.392}) ^A [Mg _{0.392} Fe _{1.558} Nd _{0.05}] ^B O ₄	410	410
0.60	0.05	(Zn _{0.60} Mg _{0.092} Fe _{0.308}) ^A [Mg _{0.308} Fe _{1.642} Nd _{0.05}] ^B O ₄	340	339
0.80	0.05	(Zn _{0.80} Mg _{0.000} Fe _{0.200}) ^A [Mg _{0.200} Fe _{1.750} Nd _{0.05}] ^B O ₄	-	-
1.00	0.05	(Zn _{1.00} Mg _{0.000} Fe _{0.000}) ^A [Mg _{0.200} Fe _{1.950} Nd _{0.05}] ^B O ₄	-	-
0.00	0.10	(Zn _{0.00} Mg _{0.124} Fe _{0.876}) ^A [Mg _{0.876} Fe _{1.024} Nd _{0.10}] ^B O ₄	623	620
0.20	0.10	(Zn _{0.20} Mg _{0.258} Fe _{0.542}) ^A [Mg _{0.542} Fe _{1.458} Nd _{0.10}] ^B O ₄	498	501
0.40	0.10	(Zn _{0.40} Mg _{0.202} Fe _{0.398}) ^A [Mg _{0.398} Fe _{1.502} Nd _{0.10}] ^B O ₄	405	405
0.60	0.10	(Zn _{0.60} Mg _{0.092} Fe _{0.308}) ^A [Mg _{0.308} Fe _{1.594} Nd _{0.10}] ^B O ₄	332	330
0.80	0.10	(Zn _{0.80} Mg _{0.000} Fe _{0.200}) ^A [Mg _{0.200} Fe _{1.700} Nd _{0.10}] ^B O ₄	-	-
1.00	0.10	(Zn _{1.00} Mg _{0.000} Fe _{0.000}) ^A [Mg _{0.000} Fe _{1.900} Nd _{0.10}] ^B O ₄	-	-

On substitution, the Nd^{3+} ion resides on octahedral B sites. This trivalent substitution causes an increase in the amount of Mg^{2+} ion occupying A sites (δ). Similar results are reported in the case of Gd^{3+} substituted Cd-Cu ferrite systems [13]. As presented in Table 2, the substitution of Nd^{3+} ion results in the reduction of the Curie temperatures.

This may be due to the Nd^{3+} ion, substituted for Fe^{3+} ion, causing reduction in Fe-Fe interaction ion on B-sites giving rise to the dilution of magnetisation of B-sites. Such reduction in Curie temperature due to rare-earth substitution in Ni-Zn ferrites have also been reported in [14]. This supports the occupancy of Nd^{3+} ion on B-sites.

Conclusion

Variation of lattice parameter a obeys Vegard's law, showing its tendency to increase with Zn^{2+} concentration. Saturation magnetisation and magnetic moment increases up to $x = 0.4$ then thereafter decreases. The substitution of Nd^{3+} ion causes reduction in saturation magnetisation and magnetic moment. The compositions for $x \geq 0.80$ show paramagnetic behaviour at and above room temperature. Cation distribution obtained from modified Upadhyay model show 0.122 of magnesium sits on A sites for $x = 0.00$. This occupancy increases up to $x = 0.20$ and decreases thereafter. The substitution of Nd^{3+} ion, causes to increase the occupancy of Mg^{2+} ion on A site.

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