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Influence of Mn-Zn Co-Substitution on the Structural and Magnetic Properties of Magnesium Ferrite

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Abstract*— The magnesium manganese - Zinc ferrites having chemical formula $MgMn_xZn_xFe_{2-2x}O_4$ for x varying from 0.0 to 0.6 in the steps of 0.1 have been synthesized by standard ceramic technique. The variation of Mn - Zn substitution has significant effect on the structural and magnetic properties of magnesium ferrite. The phase identification of the powders performed using X-ray diffraction technique shows presense of high purity cubic phase and absence of any secondary phases. The lattice constant increases from 8.35 to 8.43Å with increase in Mn-Zn substitution x. The Pulse field hysteresis loop tracer technique is used to study the magnetic properties of the prepared samples. The Saturation magnetization (M_s), remanance magnetization (M_r), Coercivity (H_c) and magneton number (n_B) are measured at room temperature. The Saturation magnetization (M_s) and magneton number (n_B) increases upto x = 0.3 and then decreases with increase in Mn-Zn substitution x in magnesium ferrite.AC Susceptibility measurement confirms the decrease in Curie temperature with increase in Mn-Zn substitution x.

Keywords*— Magnesium ferrite, ceramic technique, X-ray diffraction, Magnetization.

I. INTRODUCTION

Ferrite crystallises in spinel structure in which both divalent and trivalent is distributed among tetrahedral (A) and octahedral [B] sites. The electrical and magnetic properties of several mixed ferrites with the spinel type crystal structure have been the subject of many investigations. Ferrites have many applications in high frequency devices and they play an useful role in technological applications due to their high resistivity, low eddy current and dielectric losses over a wide range of frequencies. They are widely used in transformer core, inductor data storage and microwave devices. The basic electrical and magnetic properties can be tailor made careful control of composition and microstructure, by method of preparation [1].In ferrites, the exchange interaction aligns the magnetic moments of the ions on (A) sites antiparallel to those on the [B] sites. The interaction is called as "Fe^{3+}(A)-O-Fe^{3+}[B] superexchange interaction" which resulting in the amount of magnetization. The magnetic properties depend on the magnetic cation distribution between (A) and [B] sites in $MgFe_2O_4$.

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Magnesium ferrites have been the subject of study for a long time [2]. Magnesium ferrite is a soft magnet (space group Fd3m) with low coercivities and high resistivities. A number of researchers have studied the electrical and magnetic properties of magnesium ferrite substituted by divalent [3], trivalent [4] and tetravalent [5] ions. The simultaneous substitutions of divalent non magnetic and tetravalent magnetic cations like Zn, Mn ions in magnesium ferrites may give rise to interesting results. The basic properties of spinel ferrites are sensitive to the nature of substituent. Zn is a nonmagnetic and have strong tendency to occupy at tetrahedral (A) site whereas Mn^{4+} is magnetic in nature and prefers to occupy octahedral [B] site, Mg ions occupy both the tetrahedral (A) site and octahedral [B] sites. Therefore, it will be interesting to investigate the structural and magnetic properties of $MgMn_xZn_xFe_{2-2x}O_4$ samples.
In the present work, Mn-Zn substituted magnesium ferrite with chemical formula $MgMn_xZn_xFe_{2-2x}O_4$ (for x= 0.0 to 0.6 in the steps of 0.1) were synthesized using standard ceramic technique. The prepared samples were characterized by X-ray diffraction and Magnetization technique.

II. EXPERIMENTAL TECHNIQUE

Polycrystalline ferrite system $MgMn_xZn_xFe_{2-2x}O_4$ with composition x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6, were synthesized by standard ceramic technique. The samples were prepared by thoroughly mixing AR grade MgO, ZnO, MnO and Fe_2O_3 oxides in stoichiometric ratio and later on well grounded in a planetary agatemortar for few hours. The powder samples were presintered at 950 ˚C for 12 h in a programmable furnace and slowly cooled to room temperature. The sintered powders were mixed with 2% of PVA as a binder and uniaxially pressed at a pressure of about 6 tons $cm^{-2}$to form pellets of 10 mm diameter and 2–3 mm thickness. These pellets were finally sintered at 1100 ◦C for 12 h in a programmable furnace to remove the organic binder. The sintered samples were characterized by X-ray diffraction method. The X-ray diffraction patterns were recorded at room temperature using Cu-Kα radiation on X-Ray diffractometer (BRUKER AXS D8 Advance). The X-ray diffraction patterns were recorded in 2θ range of 20^0 to 80^0.The magnetic properties were recorded at room temperature using pulse field hysteresis loop technique. Using magnetization versus applied magnetic field (M-H plots), the saturation magnetization, coercivity, remenant magnetization of each sample was determined. The Curie temperature of the samples was measured by AC Susceptibility technique.

III. RESULTS AND DISCUSSIONS

A. Structural characterization

Fig. 1 (a,b,c) shows the X-ray diffraction patterns of pure magnesium ferrite , Mn-Zn substituted $MgFe_2O_4$ samples for x= 0.1,0.2,0.3 and x= 0.4,0.5,0.6 respectively. The entire samples under investigation shows the characteristics peaks of ferrite material with most intense peak (311). All the samples show good crystallization with well defined peaks. The peaks could be successfully indexed as (220), (311), (222), (400), (422), (511), (440) and (533) which are characteristics of single phase cubic spinel structure. The XRD patterns exclude the presence of any undesirable secondary phase.

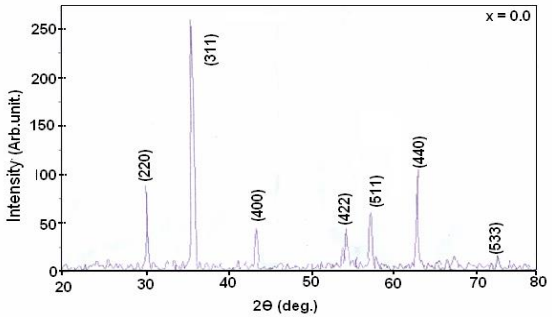

Fig.1(a) X-ray diffraction pattern for $MgMn_xZn_xFe_{2-2x}O_4$ system for x= 0.0.

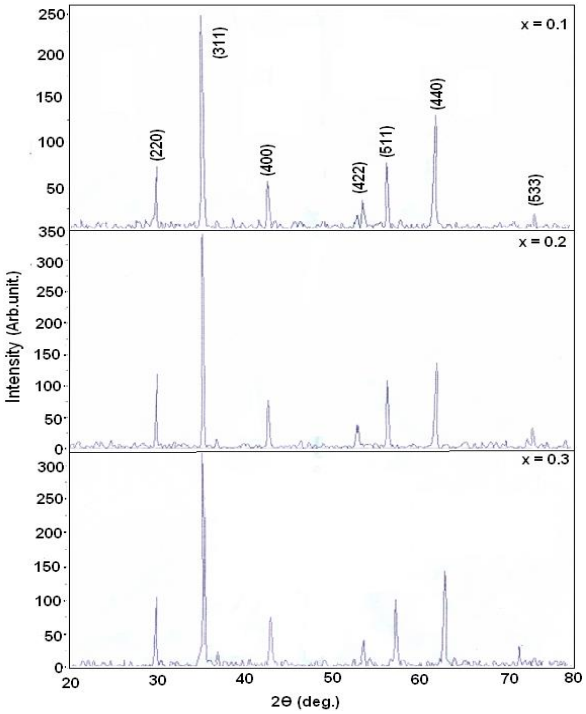

Fig.1(b) X-ray diffraction pattern for $MgMn_xZn_xFe_{2-2x}O_4$ system for x= 0.1,0.2,0.3.

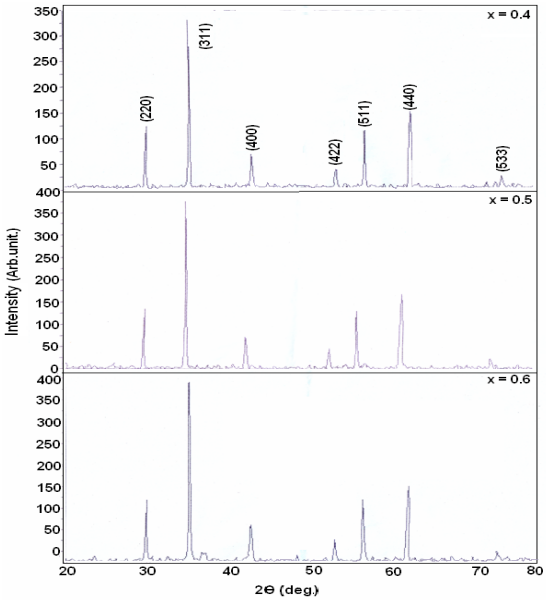

Fig.1(c) X-ray diffraction pattern for $MgMn_xZn_xFe_{2-2x}O_4$ system for x= 0.4, 0.5, 0.6.

All the peaks observed in spectra correspond to f.c.c. spinel structure. The peaks observed in the XRD patterns are sharp and intense. The XRD pattern indicates that the peak shifts towards right side due to substitution of Mn and Zn ions. This is confirmed by the change in the interplanar spacing (d) values. The values of interplanar spacing'd' are used to determine lattice constant 'a' of the spinel ferrite system. The values of lattice constant are given in table I. The lattice constant increases with increase in substitution of Mn - Zn ions and obeys Vegard's law [6]. The linear increase in lattice constant with composition is attributed to difference in ionic radii of the constituent ions. In the present series $MgMn_xZn_xFe_{2-2x}O_4$, $2Fe^{3+}$ ions are replaced by combinations of tetravalent Mn^{4+} ions and divalent Zn^{2+} ions. The average ionic radii of Mn^{4+} and Zn^{2+} is quite large than that of Fe^{3+} ions and hence the substitution of Mn, Zn ions in place of Fe^{3+} ions causes the increase in lattice constant of the $MgMn_xZn_xFe_{2-2x}O_4$ system. The X-Ray density 'd_x' for all the composition x was calculated by using the values of lattice constant 'a' and molecular weight. The values of X-ray density are given in table I. The X-ray density decreases from x= 0.0 to 0.2 and then slightly increases with increase in composition x. The bulk density (d_b) (apparent density) of all the samples was measured using Archimedes principle [7]. The values of bulk density are given in Table I. The porosity 'P' of all the samples was also determined using the values of X-ray density and bulk density. The porosity value varies from 34% to 40% which are shown in table I. The particle size of all the samples was calculated using the Scherrer formula [8]. The particle size goes on decreasing with increase in Mn-Zn substitution x and the values are given in table I.

Table: I

The lattice constant (a), X-ray density (d_x), bulk density (d_b) and porosity (%P), particle size (T) for $MgMn_xZn_xFe_{2-2x}O_4$ system.

x	a(Å)	d_x (gm/cm^3)	d_b (gm/cm^3)	% P	T (Å)

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0.0	8.35	4.562	2.821	38.09	276
0.1	8.37	4.547	2.783	38.71	276
0.2	8.39	4.542	2.744	39.65	320
0.3	8.40	4.543	2.771	38.98	304
0.4	8.41	4.545	2.870	36.89	301
0.5	8.42	4.547	2.933	35.89	307
0.6	8.43	4.550	3.001	34.83	293

B. Magnetic Measurements

Magnetic properties were measured at room temperature using pulse field hysteresis loop tracer technique.

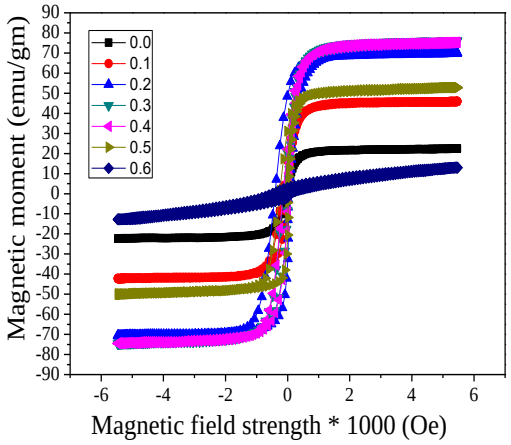

Fig.2 M-H plots recorded for $MgMn_xZn_xFe_{2-2x}O_4$ system.

The plots of magnetization versus applied field (M-H) helps in understanding the magnetic response of material and provides the useful information about the magnetic parameters such as saturation magnetization (M_S), coercivity (H_C), remanence magnetization (M_r) and magneton number. The hysteresis plots (M-H) of $MgMn_xZn_xFe_{2-2x}O_4$ system for x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 are depicted in Fig.2. The magnetic parameters were obtained using magnetization curve and are shown in table II. From the table II it is observed that the saturation magnetization (M_S) initially increases upto x= 0.3 with Mn-Zn substitution x and then decreases indicating the canted spin structure at octahedral B site. Similar results are observed in the literature [9]. Remanence magnetization (M_r) of all the samples under investigation was obtained from M-H plots and the values are presented in table II. The plot of saturation magnetization (M_s) versus applied field (H) provides the useful information regarding the domain state of the samples from the ratio of remanence magnetization to saturation magnetization i.e. M_r/M_s. The values of M_r/M_s of the present samples obtained from M-H plots are given in table II. Using M-H plots the coercivity of all the samples was obtained and the values are presented in Table II.

Table.II
Saturation magnetization (M_s), remanent magnetization (M_r), Coercivity (H_c), remanent ratio (M_r/M_s), magneton number (n_B) of $MgMn_xZn_xFe_{2-2x}O_4$ system

x	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	(M_r/M_s)
0.0	22.50	4.24	58.48	0.188
0.1	45.93	1.62	2.34	0.035
0.2	70.01	0.19	11.18	0.002
0.3	76.12	27.31	42.83	0.358
0.4	75.29	0.75	6.93	0.009
0.5	52.90	12.76	33.23	0.241
0.6	13.08	0.01	6.72	0.001

The values of saturation magnetization are used to determine the magneton number (n_B)(the saturation magnetization per formula unit in μ_B). The values of magneton number are given in table III. It can be seen from the table II and III that the saturation magnetization and magneton number both decreases in general with Mn, Zn concentration x. It is seen from table III that magneton number n_B initially increases up to x = 0.3 and then decreases with Mn-Zn concentration x. Neel's model has been applied to understand the magnetic behaviour of the present samples. According to Neel's model, magneton number n_B is given by the difference in the magnetic moment of tetrahedral (A) and octahedral [B] site i.e.

$$n_B = M_B - M_A. \quad (1)$$

The magnetic moments of A and B sites are calculated by taking the ionic magnetic moments of Fe^{3+}, Mn^{4+}, Zn^{2+}, Mg^{2+} as $5\mu_B$, $4\mu_B$, $0\mu_B$, $0\mu_B$ respectively. Using cation distribution formula the values of Neel's magnetic moments are calculated and are given in Table III. The observed and calculated magnetic moment are closely agreement with each other for x = 0.0 to x = 0.3. For x>0.3, it differ from each other indicating the existence of canted spin structure at octahedral B site. Thus, Neel's model is applicable up to x = 0.3. To understand the magnetic behaviour, above x = 0.3 Yafet-Kittel model is applied. The values of Y-K angles are given in
table III.

Table III
Magneton number 'n_B'(μ_B), Y-K angle 'θ_{YK}' and Curie temperature T_c (K) of $MgMn_xZn_xFe_{2-2x}O_4$ system.

Comp.x	Magneton Number 'n_B'(μ_B)		Y-K angle 'θ_{YK}'	Curie temp. T_c(K)
	Observed	Calculated		
0	0.81	1	0	683
0.1	1.65	1.68	0	673

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0.2	2.53	2.56	0	652
0.3	2.76	3.4	23.86	641
0.4	2.74	4.06	26.23	619
0.5	1.93	4.67	46.97	574
0.6	0.48	5.05	67.92	542

C. AC Susceptibility

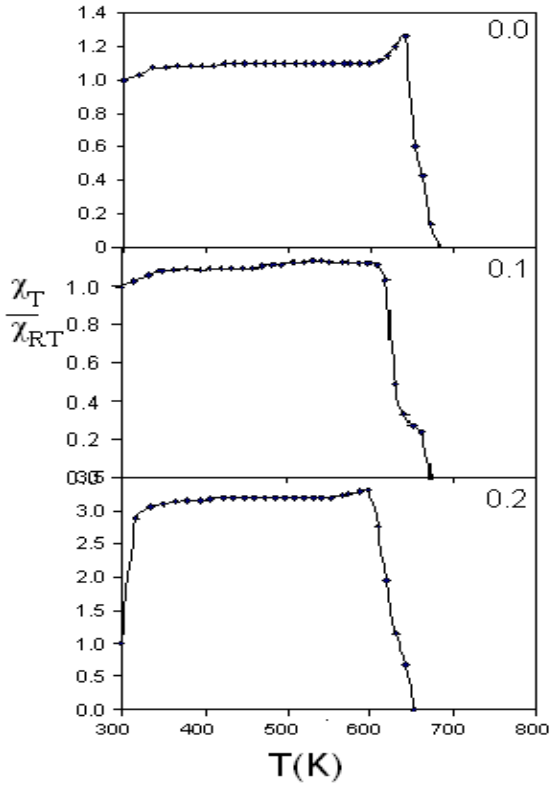

Fig. 3. Plots of χ_T/χ_{RT} versus temperature for the $MgMn_xZn_xFe_{2-2x}O_4$ system for typical samples x = 0.0, 0.1 and 0.2.

The thermal variation of AC susceptibility (χ_T/χ_{RT}) for the typical samples samples(x= 0.0, 0.1, 0.2) of $MgMn_xZn_xFe_{2-2x}O_4$ system is shown in Fig. 3.

The plots exhibit decrease in ferrimagnetic behaviour. The hump seen in the χ_T/χ_{RT} plots near the magnetic transition represents the transition of single domain to super-paramagnetic nature of the material.

Using the χ_T/χ_{RT} versus temperature plot, Curie temperature of the samples can be estimated. The values of Curie temperature deduced from susceptibility plots are listed in Table III. The decrease in Curie temperature with increase in Mn-Zn ion concentration 'x' is related to decrease in magnetic linkages associated with tetrahedral (A) and octahedral [B] sites.

IV. CONCLUSIONS

The Mn-Zn substituted $MgMn_xZn_xFe_{2-2x}O_4$ (x= 0.0 to 0.6 in the steps of 0.1) samples have been successfully synthesized by standard ceramic technique. The influence of Mn-Zn substitution on the structural and magnetic properties of magnesium ferrite has been studied. The X-ray diffraction analysis confirms the single phase cubic spinel structure for all the samples. The lattice constant increases with increase in Mn-Zn substitution x. The particle size estimated from Debye-Scherrer's formula varies in the range 276 to 320 Å. The saturation magnetization and magneton number initially increases upto x = 0.3 and then decreases indicating the existence of canted spin structure at octahedral B site. Behavior of saturation magnetization is explained on the basis of Neel's model. The AC Susceptibility technique is used to determine the Curie temperature of all the samples. The Curie temperature decreases with increase in Mn-Zn substitution x.

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