Synthesis, charactrization, catalytic properties and effect of sintering temperature on spinel ferrite synthesized by co-precipitation method

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ABSTRACT

The various compositions of MgNi ferrite system were synthesized by co-precipitation technique. The resulting powder of composition $Mg_{0.5}Ni_{0.5}Fe_2O_4$ was further heated at different temperatures from 600ºC-1000ºC for four hours to get good surface area. The formation of compound was then investigated by thermal analysis (TGA/DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The formation of spinel structure was confirmed by X-ray diffraction. The (311) peak was found to be most intense. SEM microphotographs exhibited increase in grain size with increase in sintering temperature. Unlike single oxides or their mixtures, the single phase spinel-type binary and ternary oxides show extra structural stability and exhibit interesting catalytic properties. Hence the decomposition of H_2O_2 is carried out and to calculated activation energy.

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INTRODUCTION

The spinel ferrites of formula $M^{II}Fe_2^{III}O_4$ have attracted the attention of physicists and technologists. In spinels (where, M=Mg, Ni, Co&Zn etc.) are a very important group of mixed metals. Since they cover wide range of applications such as telecommunication systems, computer memories, microwave devices, heat transfer devices etc. Ferrites prepared by various method one of them, ceramic method involving high-temperature (1100ºC). However, the method has some inherent drawbacks such as (i) poor compositional control, (ii) chemical inhomogeneity, (iii) coarse particle size and (iv) introduction of impurities during grinding. Wet-chemical methods such as co-precipitation using metal sulphates solutions digested at 100ºC, by adding 10% NaOH and thus overcome these drawbacks and produced homogeneous, and reproducible ferrite powders using aqueous solutions of salts of constituent ions. This has motivated us to synthesize the mixed solid solution series $Mg_{1-x}Ni_xFe_2O_4$[1,2].

In the past various methods are used for the preparation of spinel ferrites such as ceramic method, solvent evaporation method, hydrothermal method, citrate method, combustion method etc. Among these methods the co-precipitation method is widely used for preparation due to its overriding advantages such as composition flexibility[3,4,5].

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EXPERIMENTAL

All AR grade ingredients were weighed carefully on microbalance to have the proper stoichiometric proportion of salts required in the final ferrite powder. The compositions of $Mg_{1-x}Ni_xFe_2O_4$ was synthesized by Co-precipitation technique. The amount of each metal sulphate was dissolved in distilled water and precipitation of the hydroxides was carried out at a controlled 9.5 pH using 10% NaOH solution and was then digested on water bath for 4 hours and was oxidized by adding 75ml of 30% H_2O_2 (100Vol.) solution. To obtain fine powder, this was presintered at 100^0C for six hour in argon atmosphere[6]. The presintred powder was milled in agate motor with acetone. The samples of composition $Mg_{0.5}Ni_{0.5}Fe_2O_4$ were sintered at different temperatures from 600^0C-1000^0C.

X-ray powder diffraction patterns were recorded on Philips PW 1710 diffractometer with Cu Kα radiation using nickel filter(λ=1.5405). X-ray diffraction powder patterns of all the composition indicated formation of single phase spinel structure. The lattice parameters were evaluated by using the relation.

$$a = d \ (h^2+K^2+l^2)^{1/2} \tag{1}$$

Where notations have their usual meaning.

RESULTS AND DISCUSSION

The experimental XRD data of the ferrite sample agreed very closely with the standard values given in the JCPDS data cards thus confirming the spinel phase. XRD patterns of $Mg_{0.5}Ni_{0.5}Fe_2O_4$ was heated at different temperatures are given in figure 1 It is observed that well-defined peaks with (311) reflection appear to be more intense. The figure also shows that the peaks become sharper and narrower with increasing sintering temperature, indicating the enhancement of craystallanity. The average particle size D was calculated using employing the Scherrer formula,

$$D = 0.9\lambda/Bcos\theta$$

where, d is the mean crystallite size, λ is X-ray wavelength, B is the angular line width at half maximum intensity and θ is the Bragg's angle the size was found to be 270nm. It also shows clearly that the intensity increases with increase in sintering temperature[7,8].
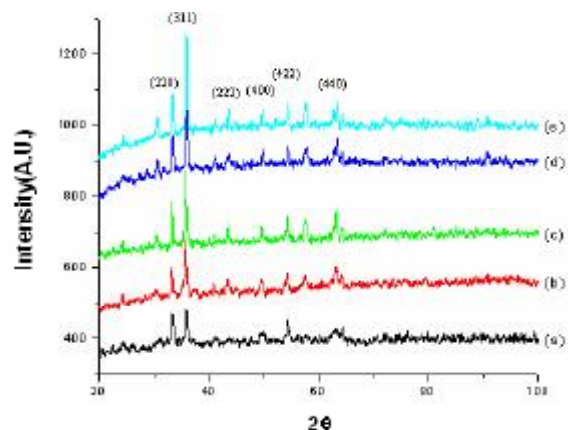

Figure 1 : XRD patterns for $Mg_{0.5}Ni_{0.5}Fe_2O_4$ ferrites sintered at (a) 600^0C (b) 700^0C (c) 800^0C (d)900^0C(e) 1000^0C
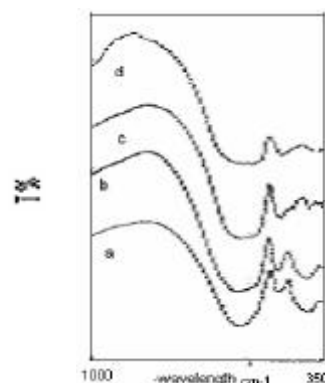

**Figure 2 : IR spectra of $Mg_{0.5}Ni_{0.5}Fe_2O_4$ sintered at (a) 1000^oC (b) 900^oC (c) 800^oC and (d) 700^oC**

Figure 2 The FT-IR spectra of different composition of MgNi ferrite shows two strong bands around $600cm^{-1}$ and $400cm^{-1}$. The spectra shown are the common characteristic features of ferrospinels. Two broad band appearing one at $600cm^{-1}$ and the other at $400cm^{-1}$ can be assigned to metal oxygen stretching frequencies. Since tetrahedral M-O bonds (Td M-O) are associated with higher force constant and lower bond lengths this stretching frequency is expected to appear at higher frequency compared to the M-O stretching frequency of octahedral (Oh M-O) sites[9].

Figure 3 shows the TGA curve for Mg-Ni ferrites. The minor weight loss before 100^0C in the TGA curve is attributed to evaporation of residual water[10]. The major weight loss from 207^0C to 700^0C and further weight loss observed upto1000^0C. The plateau 700-1000^0C on TGA curve indicates the formation of Mg-Ni ferrite as a decomposition product. It may be main-

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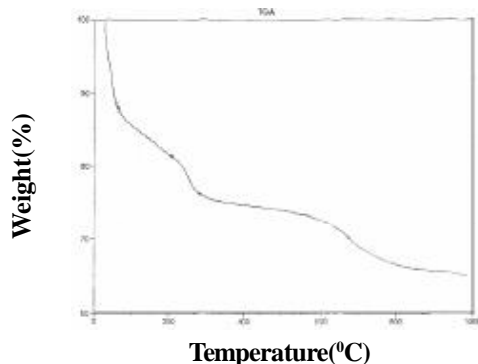
Temperature(^{0}C)
Figure 3 : TGA/DTA for system $Mg_{1-x}Ni_xFe_2O_4$
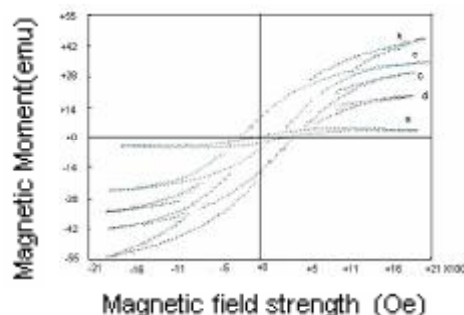
Figure 5 : Hysteresis loops reprentative of $Mg_{0.5}Ni_{0.5}Fe_2O_4$ System

(a)   **(b)**   **(c)**   **(d)**   **(e)**
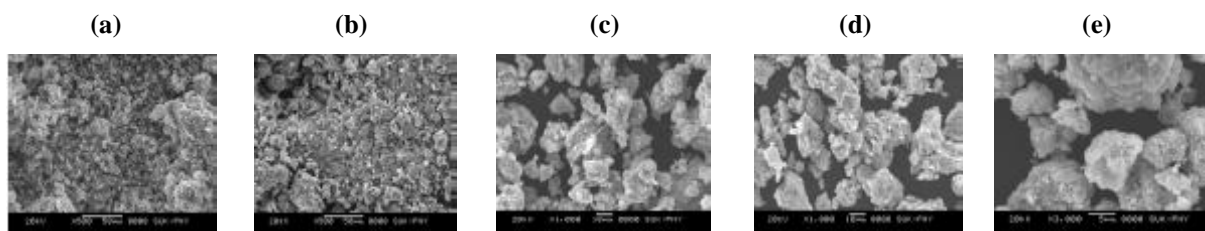
Figure 4 : SEM micrograph of $Mg_{0.5}Ni_{0.5}Fe_2O_4$ ferrites sintered at (a) 600^0C (b) 700^0C (c) 800^0C (d) 900^0C (e) 1000^0C

TABLE: 1 Magnetic hysteresis data for $Mg_{0.5}Ni_{0.5}Fe_2O_4$ system

Sr. no.	Composition	Temp. ^oC	Saturation magnetization at 300k (Ms)	Magnetic moment (n_B) (cal.)	Coersive force (Hc) (Oe)	Remanent magnetization (Mr)
1	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	600^oC	2.37	0.3478	428.57	0.4008
2	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	700^oC	11.60	1.7023	235.39	0.2379
3	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	800^oC	14.98	2.1923	222.40	0.1722
4	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	900^oC	15.04	2.2071	264.61	0.2327
5	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	1000^oC	29.76	4.3673	287.34	0.2614

tained that the formation of spinel phase is at 303^0C. Thus the temperature recorded for spinel phase formation is expected to be higher. It is observed from acetate-citrate gelatin methods that above 430^0C organics are removed completely and precipitation of particles takes place. There fore even though the decomposition is complete at 303^0C we have chosen above 500^0C as calcinations temperature.

The variation in grain size observed from SEM is plotted in figure 4 Studies of scanning electron micrographs indicated that the grain size increases with increasing temperature and sintering time. In the present, samples the grain size increases from 300nm for the sample sintered at 600^0C for 4 hours to about 400nm for the sample sintered at1000^0C. The variation in grain size calculated from scanning electron micrographs figure 4 due to increase in sintering temperature[11,12]. It is also observed that the grains are more non-linear with spherical shape.

Magnetic hysteresis

Magnetic hysteresis studies were done on samples at room temperature using alternating current hysteresis loop tracer with a field of 1 KOe. The results of magnetic hysteresis studies viz. the saturation magnetization (Ms), coercive force (Hc) and remanent magnetization are presented in TABLE 1. The photographs of the hysteresis loops obtained for compounds under investigation are given in figure 5. It was found that all the compositions of the system were ferrimagnetic at 300K[13].

The magnetic moment n_B is calculated for all compositions and the system using saturation magnetization values (Ms) by using the relation.

$n_B = Ms \times Mol.Wt. /5585$ (4)

From TABLE 1 it is observed that experimental $n\beta$ values are low as compared to the calculated $n\beta$ values[14].

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If we compare the magnetic moments of composition $Mg_{0.5}Ni_{0.5}Fe_2O_4$ at increasing temperatures, the observed values are less as compared to calculated $n\beta$ values. The low values observed for the temperature 600^0C can be attributed to magnetic interactions. In spinel mainly there are two types of magnetic exchange interactions (i) one due to direct overlap of atomic orbitals and (ii) due to the super exchange via an intermediate non magnetic ion. In this case as the cations possess electronic configuration m>S, the direct cation-cation interaction seems to be negligible.

Further in the composition $Mg_{0.5}Ni_{0.5}Fe_2O_4$ the observed magnetic moments and calculated magnetic moments values closely agree indicated that in these compounds Neels model (where moments at A-site cancels the moment at B-site) is being obeyed. The saturation magnetization of the samples increases with increase in temperature. This may be due to the relatively high orbital contribution of Ni^{2+} ions to the magnetic moment, which gives large induced anisotropy. The ratio of remnant magnetization to saturation magnetization (MJ/M s) value for most of the samples heated up to 600^0C is marginally higher than 1000^0C.

TABLE 2 : Activation energy for spinel oxides

Sr.no.	Composition	Temperature range (^{O}C)	Rate constant x 10^{-3}	Activation energy (KJ /Mol)
1	$MgFe_2O_4$	50	5.4776	59.39
		60	10.6358	
2	$Mg_{0.75}Ni_{0.25}Fe_2O_4$	50	3.6869	33.51
		60	5.3555	
3	$Mg_{0.5}Ni_{0.5}Fe_2O_4$	50	6.9753	13.13
		60	7.6051	
4	$Mg_{0.25}Ni_{0.75}Fe_2O_4$	50	4.9123	48.57
		60	8.4523	
5	$NiFe_2O_4$	50	5.5119	25.48
		60	6.7959	

Catalytic properties

Decomposition of H_2O_2 by spinel oxides of the system $Mg_{1-x}Ni_xFe_2O_4$:

The decomposition of H_2O_2 was studied at different temperatures from 50^0C and 60^0C and the rate constants were calculated using the relation

$$K = 2.303 \log (a/a-x)/t \tag{2}$$

Where, a = initial concentration of H_2O_2 and a-x = concentration of H_2O_2 at time t. The rate of decomposition was found to obey the first order rate law. It is found that decomposition of H_2O_2 increases with increase in temperature. The activation energy values were calculated using rate constants at different temperatures by the relation[15].

$$E = 2.303 \log(K_2/K_1) \times Rx\ T_1xT_2/ T_2\text{-}T_1 \tag{3}$$

Where K_1 and K_2 are the rate constants at temperatures T_1 and T_2 respectively. Further it is observed that (TABLES 2 and 3) as the rate constant decreases percentage decomposition of H_2O_2 increases. Further it is also observed that catalytic activity of spinels increases with increase in temperature.

In the case of spinels, the catalytic activity is due to the mixed oxides involving oxidation reduction process. The oxides which are capable of showing variable oxidation states are found to be better catalysts[16]. The rate of decomposition of H_2O_2 was found to obey first order rate law for the compositions of the system at temperature from 50^0C to 60^0C. The rate constants and decomposition at different time intervals for the different compositions of the system are given in TABLES 2 and 3.

Further it is observed that at composition $NiFe_2O_4$ the decomposition of hydrogen peroxide is found to be more active as compared with composition $MgFe_2O_4$. This can be explained on the basis of activation energy.

TABLE 3 : Catalytic effect of $Mg_{1-x}Ni_xFe_2O_4$ system on the decomposition of H_2O_2 at 50 and 60^0C

Composition	Temp. ^{o}C	Rate constant(k)	% Decomposition of H_2O_2					Activation energy
			60m	120m	180m	240m	300m	
$MgFe_2O_4$	50	5.4776	33.0	51.28	58.97	71.79	59.39	59.39
	60	10.6358	61.53	74.35	79.48	87.17	92.30	
$Mg_{0.75}Ni_{0.25}Fe_2O_4$	50	3.6869	43.58	48.71	53.84	58.87	66.66	33.51
	60	5.3555	38.46	46.15	53.84	61.53	76.92	
$Mg_{0.5}Ni_{0.5}Fe_2O_4$	50	6.9753	38.46	58.87	64.10	76.92	87.17	13.13
	60	7.6051	51.28	61.10	69.23	74.35	79.48	
$Mg_{0.25}Ni_{0.75}Fe_2O_4$	50	4.9123	30.76	41.02	53.84	61.53	82.01	48.57
	60	8.4523	58.97	64.10	71.79	76.92	82.03	
$NiFe_2O_4$	50	5.5119	35.89	46.15	51.28	58.97	79.48	25.48
	60	6.7959	46.15	53.84	61.35	74.35	84.61	

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It is observed from TABLE 1 that activation energy decreases from $MgFe_2O_4$(59.39KJmol^{-1}) to $NiFe_2O_4$ (25.48 KJmol^{-1})[17] As the catalysis involves transfer of electrons/holes from the surface of the catalyst to the substrate molecule and is reversible, the greater the activation energy, the more energy is required for electronic transition and consequently less will be the catalytic activity[18].

The catalysis performance data of various catalysts of the system $Mg_{1-x}Ni_xFe_2O_4$ on the basis of rate constant measurements at temperature (50^0C to 60^0C) is presented in TABLE 1. As the concentration of Ni^{2+} ions in the system $Mg_{1-x}Ni_xFe_2O_4$ increases, the Ni^{2+} ions enter the octahedral site, since they have got strong preference for octahedral coordination[19]. Out of the ions viz. Cu^{2+}, Fe^{3+} and Ni^{2+}, nickel ions strongly prefer octahedral site (site preference energy value of Ni^{2+} is +9 KCal/gm.At.wt. as compared to Fe^{3+} -13.3 KCal/gm.at.wt.). Since Ni^{2+} possesses more stable +2 oxidation state, hopping of charge carriers between Ni^{2+} and Fe^{3+} decreases releasing less no of electrons for chemical reaction. Therefore catalytic activity decreases from percentage of Ni (x=1to0).

CONCLUSIONS

It has been concluded that fine grain of Mg Ni ferrite powder can be synthesized by using Co-precipitation method. This method requires low temperature and short time period for preparation. All the compositions of the system $Mg_{1-x}Ni_xFe_2O_4$ showed single cubic phase as observed by X-ray powder diffraction technique. Scanning Electron micrographs indicated increase in grain size with increase in temperature. Infrared spectral studies indicated two strong absorption bands one around 400cm^{-1} and the other around 600cm^{-1}.

Thermal analysis was carried out to determine thermokinetic parameters. Magnetic hysteresis measurements indicated that all the compositions are ferrimagnetic. Saturation magnetization, magnetic moment, coercive force and remanent magnetization showed increasing trend with increase in temperature concentration.

Catalytic study for the decomposition of H_2O_2 is maximum at composition $NiFe_2O_4$. This is attributed to the increasing activation energy and availability of less active site on the surface of the catalyst as the concentration of Nickel increases.

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