

SYNTHESIS AND CHARACTERIZATION OF $Ni_{1-x}Mg_xFe_2O_4$ NANOFERRITES BY SUCROSE METHOD

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Abstract: The nanoferrites with general formula $Ni_{1-x}Mg_xFe_2O_4$ ($0.0 \leq x \leq 0.5$) were synthesized by sucrose method (chemical method). Sucrose solution provides wrapping through co-ordination for the cations in solution and works as chelating agent and it behaves as a fuel for combustion reaction by oxidation of nitrate ions. The formation of cubic structure of nanoferrites were confirmed using X-ray diffraction analysis. The particles size estimated by Debye-Scherrer formula and it is found in the range from 41nm to 46nm. The increase of lattice constant with increase in Mg concentration was due to the various ionic radii of the elements. The absorption bands assigned around $420cm^{-1}$ and $580cm^{-1}$ belongs to the stretching of vibrational complexes of octahedral and tetrahedral sites of the ferrites respectively. The bond length of octahedral site and tetrahedral site was found to be increases from 2.0451Å and 1.8815Å with increase in nickel concentration in ferrites.

Keywords: Absorption bands, lattice constant, particles size, porosity and X-ray diffraction.

Introduction: Nanophase and nanostructured ferrite materials are found to have wide potential applications in the field of nanosciences, optics and electronics. The unique properties of nanomaterials are determined by their size, surface structure and interparticle interactions [1]. The miniaturization trends of electronic devices resulted in the development of new devices called multilayer ferrite chip inductors (MLFCI) [2]. Ferrite chip inductors are one of the important components for the latest electronic products such as cellular phones, video cameras, notebook computers, hard and floppy drives, etc. Ferrite materials exhibit ferrimagnetism due to the super exchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to ferromagnetic materials where the spins are parallel. This enables the ferrite to find applications at higher frequencies and makes it technologically very valuable.

In the present study, $Ni_{1-x}Mg_xFe_2O_4$ ferrites ($0.0 \leq x \leq 0.5$) were synthesized by sucrose method. Ferrites were characterized by X-ray diffraction and FTIR spectroscopy. Using this method, the particle size of synthesized nanoferrites found to be around 41nm to 46nm.

Preparation Method: About 10gm of polyvinyl alcohol (PVA) was dissolved in 100ml deionized water using magnetic stirrer. Dissolve 30gm of sucrose in 50ml deionized water and stir to get the clear solution. 10ml of 10% PVA solution was added to the hot sucrose solution as obtained. It is then heated, stirred to get clear solution.

The metal nitrates with high purity AR grade materials like $Ni(NO_3)_2$, $Mg(NO_3)_2$ and $Fe(NO_3)_3$ are the starting materials for the preparation. These nitrates were taken according to the formula in a stoichiometry proportions and dissolved in 50ml

deionized water to get the homogeneous mixture. To this solution, above prepared PVA and sucrose solution were added and heated on a magnetic stirrer at a suitable temperature until NO_2 fumes disappear to form a viscous mixture (or black gel). This viscous mixture was then heated on a electric or gas burner till the powder began to burn like live charcoal undergoing oxidation to form nanoferrites in powder form. The ferrite powder was pre-sintered at $800^\circ C$ for 8 hours in a programmed muffle furnace and cooled to room temperature. To this powder, 2% of PVA were added because it behaves like a binding agent and then pressed into the pellet form. These pellets were sintered finally at $1000^\circ C$ for 12 hours and these pellet samples were cooled at room temperature due to the homogenization of the composition, densification and grain growth simultaneously.

Results and Discussions: X-ray diffraction

Studies: The formation of cubic spinel structure of $Ni_{1-x}Mg_xFe_2O_4$ nanoferrites were confirmed by X-ray diffraction analysis using X-ray diffractometer (model: Image plate MAR345, RRCAT Indore) of energy 15keV with the wavelength of 0.80034\AA . Using synchrotron radiation source, maximum peaks were identified and indexed with the help of ASTM datas.

Non-observation of extra peaks in the plot shows the purity of the materials. No other phase/ impurities were detected in ferrites [3]. The particles size were estimated by debye-Scherrer formula using maximum intensity peak (i.e. (311) and which is found in the range from 41nm to 46nm as shown in figure 2.

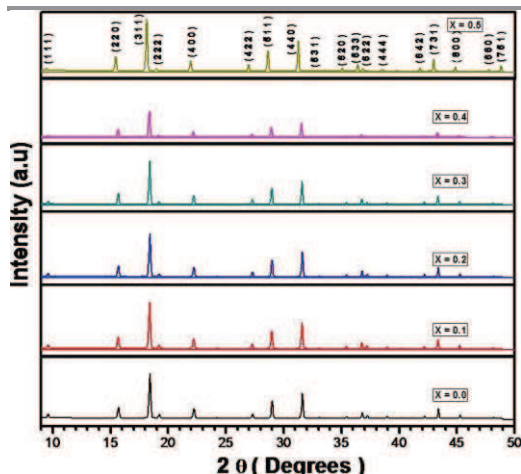


Figure 1. X-ray diffraction plot of Ni_{1-x}Mg_xFe₂O₄ (0.0 ≤ x ≤ 0.5).

The variation of particle size mainly depends upon the chemical composition, rate of reaction, annealing conditions, annealing time, etc [4]. It was observed that the particles size increases with increase in temperature due to the formation of the ferrite grains, better stabilization and growth of the ferrites.

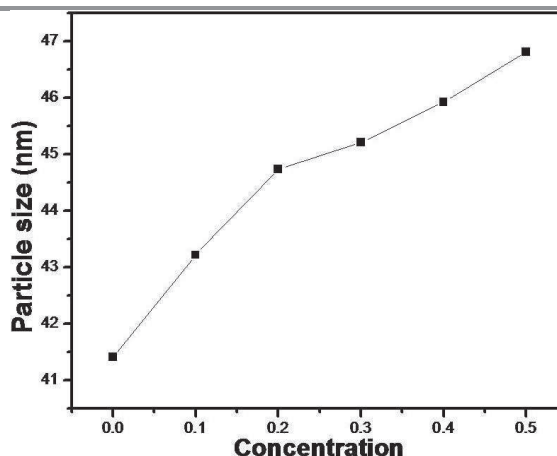


Figure 2. Variation of particle size with concentration of Ni_{1-x}Mg_xFe₂O₄ (0.0 ≤ x ≤ 0.5)

The lattice constant found to be increases with increase in magnesium concentration in nickel ferrites was due to variation in ionic radii of the elements. The Ni²⁺ ion have the ionic radii of (0.069nm) and Fe³⁺ (0.0645 nm) ions and Mg²⁺ have the ionic radii of (0.072nm).

Table.1 Particle size, lattice constant, absorption bands, %porosity, force constants, bond length and ionic radius.

X Composition	Particle size (nm)	Lattice constant (a)	Absorption Bands (cm ⁻¹)		% Porosity	Force constants (Nm ⁻¹) x 10 ²		Bond Length (Å)		Ionic Radii(Å)	
			v ₁	v ₂		K _o	K _t	R _A	R _B	r _A	r _B
NiFe ₂ O ₄	41.41	8.6138	412	603	15.15	4.25	0.2123	1.8815	2.0451	0.645	2.82
Ni _{0.9} Mg _{0.1} Fe ₂ O ₄	43.22	8.3035	424	593	15.48	4.01	0.2051	1.8818	2.0525	0.6525	2.87
Ni _{0.8} Mg _{0.2} Fe ₂ O ₄	44.74	8.3117	418	586	17.55	3.77	0.1996	1.8821	2.0611	0.66	2.90
Ni _{0.7} Mg _{0.3} Fe ₂ O ₄	45.21	8.3139	422	584	18.83	3.53	0.1977	1.8826	2.0675	0.6675	2.93
Ni _{0.6} Mg _{0.4} Fe ₂ O ₄	45.93	8.3963	424	583	19.40	3.29	0.1965	1.8831	2.0751	0.675	2.95
Ni _{0.5} Mg _{0.5} Fe ₂ O ₄	46.82	8.3963	426	582	20.72	3.05	0.1955	1.8837	2.0825	0.6825	2.98

The porosity of these ferrite nanoparticles were estimated by using Hendricks and Adam’s method [5], which is found to be increases with increase in Mg content in ferrites. The maximum porosity of nanoferrites found to be around 20.72% of Ni_{0.5}Mg_{0.5}Fe₂O₄.

FTIR Studies: The stretching of vibrational complexes of the ferrites was studied using Fourier Transform Infrared Spectroscopy (FTIR) plot as shown in figure 3. The absorption bands assigned around 420cm⁻¹ and 580cm⁻¹ belongs to the stretching of vibrational complexes of octahedral and tetrahedral sites of the ferrites respectively. The cubic spinel structure of the ferrites crystallizes in fcc (i.e. face centered cubic structure) with the space group of Fd_{3m}-O_h⁷ [6]. The vibrational frequency of the ferrites mainly depends upon cation mass, cation distribution, cation oxygen bonding forces, distance and parameters of the unit cell. The distributions of cations of the ferrites are determined by comparing

the values of observed X-ray diffraction intensity for the planes sensitive to the variation in cation distribution for the present system i.e.

$$[Mg_xFe_{1-x}]^A [Ni_{1-x}Fe_{+x}]^B \cdot O_4^2 \tag{2}$$

The force constants of the ferrites estimated using the relations,

$$K_t = 7.62 \times M_1^2 + v_1^2 \times 10^{-7} \text{ Nm}^{-1} \tag{3}$$

$$K_o = 10.2 \times (M_2^2/2) \times v_2^2 \times 10^{-7} \text{ Nm}^{-1} \tag{4}$$

where K_t and K_o are the force constants of tetrahedral and octahedral sites, M₁ and M₂ are the molecular weights of the two sites, v₁ and v₂ are the absorption bands of the sites [7].

The force constants of the tetrahedral and octahedral sites are the second derivative of potential energy with respect to site radius, the other parameter being kept constant. According to Waldron [8], the force constants were estimated using equation (3) and (4) and are listed in table 1. It is observed that the force constants of the tetrahedral and octahedral sites increases with increasing the Mg content in ferrites.

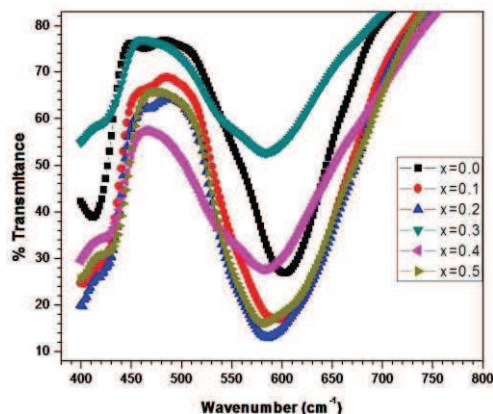


Figure 3. IR Absorption spectra of Mg substituted Nickel ferrites.

The values of bond lengths (R_A , R_B) and ionic radii (r_A , r_B) of tetrahedral and octahedral sites obtained as a test of validity of interpretation from the observed values of lattice constants of Mg ferrites and these values were listed in table 1. The bond lengths of tetrahedral site was found to be increases from 1.8815\AA with increasing nickel concentration in ferrites, similarly for octahedral site increases from 2.0451\AA . Thus, ionic radii of the tetrahedral and

octahedral sites increases with increasing nickel concentration in Mg ferrites as listed in table 1 [9].

Conclusions: The nanoferrites were successfully synthesized using chemical method or sucrose method. The particle size estimated from debye-Scherer formula were found in the range of 41nm to 46nm and which is found to be increases with respect to Mg concentration. The increase of lattice constant with increase in Mg concentration was due to the various ionic radii of the elements present in ferrites nanoparticles. The octahedral and tetrahedral sites of nanoferrites were assigned around 420 and 580cm^{-1} was due to the stretching of vibrational complexes. Bond lengths and ionic radii of tetrahedral and octahedral sites of nanoferrites were found to be increases with respect to Mg concentration.

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