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Temperature Dependent Structural and Magnetic Behaviour of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ Nano-ferrite via Citrate Method

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ABSTRACT

In the present work, magnetic nanoparticles of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite were synthesized using citrate precursor method. These nanoparticles were sintered at different temperatures ranging from 300^0C to 1000^0C. Structural studies were carried out with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Single-phase formation of spinel structure with cubic symmetry has been confirmed from the XRD patterns. The particle size and distribution was further checked by transmission electron microscope (TEM).Formation of spinel structure was confirmed from the spectra of FTIR. The investigation shows the increase in particle size with the increase in annealing temperature. The M-H loop at room temperature has been traced using vibrating sample magnetometer (VSM). The absence of magnetic parameters such as remanent magnetization, coercivity, hysteresis of the M-H curve and non zero magnetic moments indicate the existence of superparamagnetism in the magnetic nanoparticles.

Keywords: Ferrite; superparamagnetism; structural properties.

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1. INTRODUCTION

Ferrite materials have been under intense research for so long due to their useful electromagnetic characteristics for a large number of applications. Recently the synthesis and characterization of nano sized ferrite particles have attracted a lot attention of scientists and technologists because the physical and chemical properties show revolutionary modifications in the nano regime. Among the different spinel ferrites, Ni-Zn ferrites are the most adaptable magnetic materials for general applications. They can be used in microwave devices, power transformers in electronics, antennas rods, read/write heads for high speed digital tape etc [1-3]. Also, the magnetic properties of diamagnetically substituted ferrite (Ni–Zn) are of interest in low and high frequency applications. Ni–Zn ferrites are preferred at high frequencies (10–500 MHz) because of their high resistivities and low eddy current loss which can be used as a core material in transformers [4]. They have high Neel temperature (>500^0C) and tailorable magnetic inductions [5]. The Ni-Zn ferrite system (soft ferrite) has a cubic spinel configuration with unit cell consisting of eight formula units of the form $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$. Ni-Zn ferrite is a mixed spinel in which tetrahedral (A) sites are occupied by Zn^{+2} due to their readiness to form covalent bonds involving sp^3 hybrid orbitals and the octahedral (B) sites are occupied by Ni^{+2} because of their favourable fit of charge distribution of this ion in the crystal field of octahedral site [6].

In the present work, the auto-combustion citrate precursor method was used to prepare Zn doped Ni nano-ferrite. The merits of this method over conventional ceramic method was reported by E.E. Sileo et al.[7].

2. EXPERIMENTAL DETAILS

2.1 SYNTHESIS METHOD

Synthesis of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite nanoparticles was done by citrate precursor method by taking nickel nitrate ($Ni(NO_3)_2.6H_2O$, 99% pure), zinc nitrate ($Zn(NO_3)_2.4H_2O$, 99% pure), ferric nitrate ($Fe(NO_3)_3.9H_2O$, 99% pure) and citric acid ($C_6H_8O_7$, 99% pure) as starting materials. The aqueous solutions of citric acid, iron and metal salts are prepared separately in stoichiometric proportions by dissolving them in double distilled water and then mixed

together with constant magnetic stirring. The molar ratio of salt solutions with cations to citric acid was taken 1:1. The solutions were then heated at 80^0C-85^0C with continuous stirring for 2 hours. After evaporation of water the liquid converted into a homogeneous brown coloured gel (viscous solution). The viscous solution was dried in an oven overnight (≈ 15 hour) at 110^0C to form the precursor material. The precursor material was then gently crushed with mortar and pestle to get precursor powder. Obtained precursor powder was annealed at different temperatures i.e. at 300^0C, 600^0C, 800^0C and 1000^0C for 1 hour for further crystallization.

2.2 CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) patterns of the samples were taken on PANALYTICAL instrument (X'pert pro) using Cu-K_α (λ= 1.54060 A°). TEM analysis of the sample was done with Hitachi (H-7500). FT-IR spectra were recorded in KBr medium in the range of 4000-375 cm^{-1} with a IR Prestige-21 FT-IR (Model SHIMADZU-8400S). Magnetization measurements were made on Vibrating Sample Magnetometer (VSM) (PAR 155 Model) at room temperature upto 9 KOe.

3. RESULTS AND DISCUSSIONS

3.1. XRD STUDY

XRD patterns of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nano-ferrite samples at different temperatures i.e. at 110^0C (i.e. precursor powder), 300^0C and 600^0C with cations to citric acid molar ratio of 1:1 are shown in fig.1.Experimental data obtained from XRD for (311) diffraction peak are shown in table 1. From fig.1, it is clear that all the samples have face centered cubic spinel structure due to the presence of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1),(4 4 0) reflection planes[8].

The lattice constant (a_0=8.39Å) of the nano-ferrite annealed at 300^0C is found to match well with (Ni, Zn)Fe_2O_4 (8.399Å, JCPDS card no.08-0234). It can be seen that no change in the crystal structure occurs. The only effect is the X-ray line broadening decreasing with increasing annealing temperature due to growth of nano crystallites at higher temperatures. The peaks in the XRD pattern of the sample annealed at temperature 600^0C are very sharp as compared to sample annealed at 300^0C and peaks for sample formed at 300^0C are sharper than the sample at 110^0C as expected for nanocrystalline materials. This confirms the particle size increasing as the temperature goes on increasing. The increase in sharpness of XRD peaks with the increase in sintering temperature indicates the growth in crystallite size. Diffraction peaks in the X-ray diffraction patterns are highly broadened indicating the small crystalline sizes of the samples. The average crystallite sizes have been calculated (shown in table 1) from the X-ray peak broadening diffraction peaks using Scherrer's formula [9]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the crystalline size in nm, λ the radiation wavelength (1.54060 Å for Cu-K_α), β the bandwidth at half-height, and θ is the diffraction peak angle. The particle size of these samples is found to be less than 15.56 nm i.e. varies from 10.39 nm to 15.56 nm depending on annealing temperatures. The lattice constant a_0 has been calculated from eq.2 [9] for all the samples.

$$a_0 = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (2)$$

where a_0 is the lattice parameter of the unit cell, d_{hkl} is the interplanar separation, and (h k l) are the Miller indices of the plane. The calculated values of lattice constant for different annealing temperatures are given in table 1. From table 1, it can be clearly seen that with increasing temperature, lattice constant remains almost constant but particle size increases sharply first and then becomes constant. The X-ray density, d_x, is estimated by the eq.3 [10]:

$$d_x = \frac{8M}{Na_0^3} \qquad (3)$$

where M is the molecular weight, N is the Avogadro Number and a_0 is the lattice constant. Each cell has 8 formula units. It can be seen from table 1 that X-ray density decreases with increasing annealing temperature.

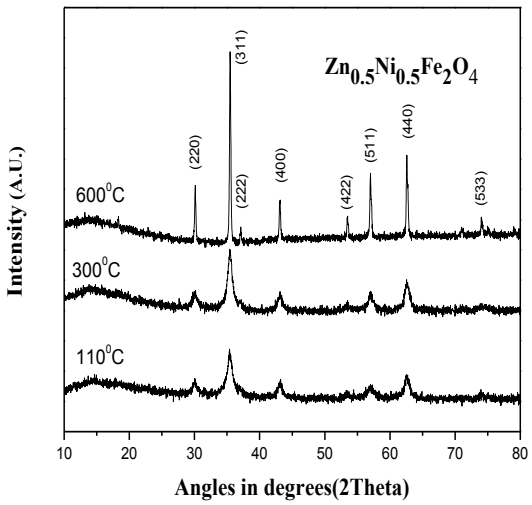

Fig.1: X-ray diffraction patterns of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nano-ferrite at different temperatures.

Table 1: Peak Position, d_{hkl} -spacing, FWHM, lattice constant, particle size and X-ray density of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ system annealed at different temperatures.

Temp.	Peak Position (2θ in degree)	d_{hkl}-spacing (Å)	FWHM (degree) (β)	Lattice constant (Å) (a_0)	Particle size (nm) (D)	X-ray density (g/cm^3) (d_x)
110	35.4746	2.53054	0.8029	8.39	10.4	5.3413
300	35.4452	2.53257	0.5353	8.40	15.6	5.3284
600	35.4328	2.53343	0.5353	8.40	15.6	5.3228

3.2. TEM STUDY

Only XRD study seems not very sensible for close and small sizes ferrite. Since particle sizes have some size distribution and also XRD line widths are affected by factors other than the particle size broadening. In order to verify the average particle size TEM analysis are also made for one sample. The sample with x=0.5 annealed at 800^{0}C for 1 hour yield an average particle size ~9.96 nm-16 nm from TEM analysis (fig.2).

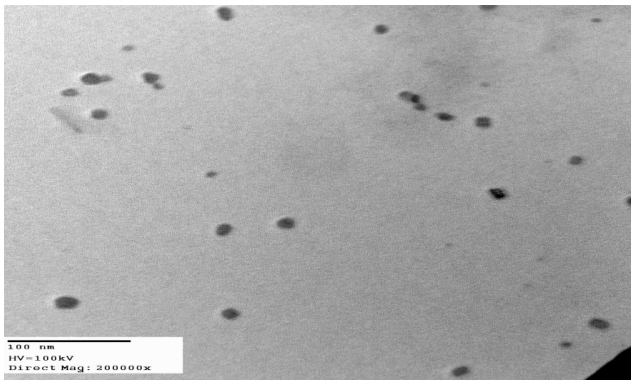

Fig.2: TEM of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite annealed at 800^{0}C for 1 hour.

3.3. FTIR STUDY

The FT-IR spectra of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nano-ferrite samples with cation to citric acid molar ratio of 1:1 and at different temperatures i.e. at 110^{0}C, 300^{0}C, 600^{0}C, 800^{0}C and 1000^{0}C are shown in fig.3. The presence of the bands in the range 375-600 cm^{-1} in the spectra confirms the formation of spinel phase [11-12]. Some additional bands around 3400-3200 cm^{-1}, 1200-1500 cm^{-1}, 1500-1700cm^{-1} and 2100-2400cm^{-1}are also present in the FT-IR spectra of the samples. These bands correspond to the stretching and bending modes of –OH group, C-H bond bending in plane mode, N-H bond in bending mode and C≡C bond in stretching mode respectively. From these results it appears that hydroxyl groups are retained in the samples during preparation of the spinel ferrites by citrate precursor method and is not completely removed even after annealed at 300^{0}C for 1 hour. It can be noticed from fig.3 that the amount of hydroxyl group in the sample annealed at 800^{0}C for 1 hour is much less than in the samples annealed below this temperature. This suggests that hydroxyl group is gradually removed as the annealing temperature is increased. The bands around 3400-3200 cm^{-1} are absent in the spectra of the sample annealed at 1000^{0}C, implying that hydroxyl is completely removed when the sample is annealed at temperature greater than 800^{0}C. The bands around 1200-1500cm^{-1} and 1500-1700cm^{-1} are decreased in the spectra of the sample annealed at 1000^{0}C for 1 hour, implying that N-H and C-H groups are not completely removed even though the sample is annealed at temperature 1000^{0}C. It is observed that the band around 2100-2400cm^{-1} i.e. C≡C remains as such in the sample even after annealing at 1000^{0}C for 1 hour.

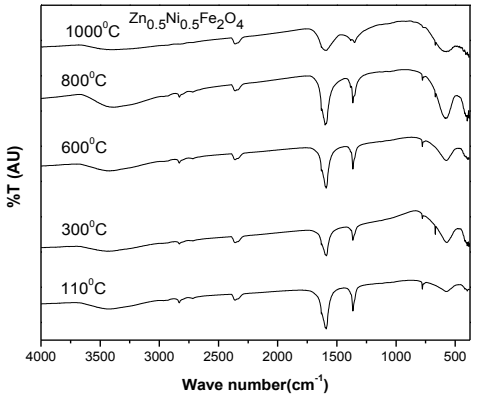

Fig.3. FT-IR spectra of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nano-ferrite prepared at different temperatures.

It is found that as the temperature is increasing the lower frequency goes on increasing from 378.908cm^{-1} to 394.773cm^{-1} and the higher frequency goes on increasing from 567.428 cm^{-1} to 583.430cm^{-1}. The little change in the values of frequencies is observed which may be due to the distribution of cations at tetrahedral and octahedral sites. In other words the change of frequency takes place due to dimensional changes in the bond lengths of the corresponding sites.

3.4. VSM STUDY

In fig.4, we present the magnetization measurements as a function of applied magnetic field for the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nano-ferrite at different temperatures i.e. 800^{0}C and 110^{0}C. It can be visualized from this figure that the sample annealed at 800^{0}C exhibits a saturation magnetization (M_S) of 77.4275emu/g, which is much higher compared with that of the sample obtained at 110^{0}C (26.4542emu/g) which is due to improved crystallinity. Thus the particle size has been found to influence the magnetic properties of materials. Saturation magnetization decreases with decreasing crystallite size of nano particles which is due to thermal fluctuations. Magnetic properties such as saturation magnetization of the nano-ferrite obtained after overnight heating at 110^{0}C are much lower than that of bulk materials and the values are also varies from method to method. Since the nanoparticles possess a large surface to volume ratio, the surface disorder phase and non-magnetic layer would reduce the magnetization behavior of the material. It can be seen from fig.6 that magnetic properties of nano sized particles are largely depended on their crystallinity which is consistent to the work of Wang [13]. The samples show zero value of retentivity and coercivity at room temperature which confirms the presence of superpara-magnetism in the prepared samples. It can be seen that saturation magnetization increases with increasing temperature.

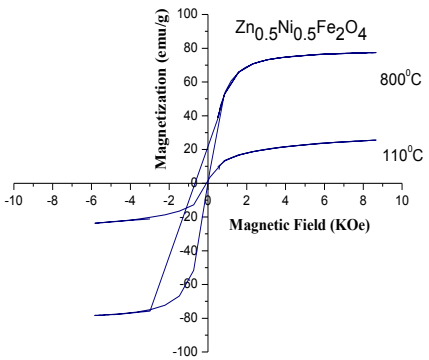

Fig.4. Magnetic hysteresis loop of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite annealed at different temperatures.

In the present study, the increase in magnetization with the increase in sintering temperature could be understood as a result of the increase in particle size and thereby the change in degree of inversion parameter, i.e. there are more Ni^{2+} ions occupying A-sites and also more Zn^{2+} ions occupying B-sites in smaller Ni-Zn ferrites resulting in lower magnetization for those samples. The retentivity and coercivity of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite annealed at 800^{0}C for 1 hour are found 21.88emu/g and 0.67KOe respectively.

CONCLUSIONS

From the overall study it can be concluded that the zinc doped nickel nano-ferrites can be successfully synthesized in pure single phase using citrate precursor method and size of the ferrite can be controlled by temperature. It is found that Zn doped Ni nano-ferrites display characteristics of superparamagnetism i.e absence of hysteresis, remanence, and coercivity at room temperature. The particle size increases with increasing annealing temperature which is clear from XRD patterns and TEM. TEM analysis shows that the ferrites prepared lie in nanoregime.

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