Dey Sanjib, IJSRR 2018, 7(3), 1106-1116

Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Investigations on $Ni_{1-x}Zn_xFe_2O_4$ (x=0.2 0.4, 0.6 & 0.8) nanoparticles synthesized by Co-precipitation and Sol-gel methods.

Dey Sanjib[*]

Department of Chemistry, Y.S. Palpara Mahavidyalaya, Palpara 721458, Purba Medinipur, India

ABSTRACT

$Ni_{1-x}Zn_xFe_2O_4$ (x= 0.2, 0.4, 0.6 and 0.8) were synthesized by co-precipitation and sol-gel method. X-ray diffraction data of the samples prepared by co-precipitation method sintered at 773K shows the formation of single phase spinel oxides having average crystallite size between 12- 15 nm and particle size by TEM measurement is 23 nm. The samples prepared by sol-gel method having crystallite size between 18-28 nm and particle size is 35 nm. X-ray diffraction pattern also shows that sol-gel prepared samples are more crystalline than samples prepared by co-precipitation method. Differential thermal analysis and thermo gravimetric measurements show that the spinel phase is formed around 523K. In co-precipitation I used constant P^H during preparation which controlled the size and agglomeration of particles and in sol-gel method uncontrolled agglomeration and layer thickness of citrate gel may lead to large particles.

KEYWORDS: Ni-Zn Ferrite, Co-precipitation, Sol-gel, Crystallite size, Particle size, Agglomeration

***Corresponding author**

Dr. Sanjib Dey

Assistant Professor,

Department of Chemistry,

Y.S. Palpara Mahavidyalaya,

Palpara Purba Medinipur, 721458, India

E-mail- deysanjib2012@yahoo.in

INTRODUCTION

Nanosized spinal ferrite particles are soft magnetic materials having structural formula of MFe_2O_4 (M = divalent metal ion e.g. Co, Ni, Mn, Cu, Mg etc). They are one of the most attracting and important properties such as low melting point, high specific heat, large expansion coefficient, low saturation magnetic moment etc[1-2]. Due to these properties the spinal ferrites have many applications such as in catalysis, sensors, nano devices, microwave devices etc[3-6]

The unit cell of spinal ferrite is composed of 32 oxygen atoms in cubic closed packed arrangement distribution in tetrahedral (A) and octrahedral sites (B) the type of cations and there distribution between to interstial sites in spinal ferrites produce many interesting magnetic properties magnetic nanoferrite particles have broad range applications such as catalytic applications[7], drug delivery[8], magnetic resonance imaging and sensing[9].

Doping ferrite nano crystals with various metals such as zinc, copper, cobalt, chromium, manganese are usually used to improve some of their electric or magnetic properties[10-12]. Zinc substitution has a remarkable influence in the magnetic properties of a nano scale system[13]. The conventional ceramics methods for the preparation of ferrite required high temperature, long time of heating and have higher grain size[14-15]. There are several experimental methods have been used in the production of nano particles like sol gel method[16] co- precipitation[17], hydrothermal method[18-19], micro wave sintering method[20], refluxing method[21], reverse micelle method[22], auto combustion method[23]. Out of these all methods co-precipitation and sol gel method have promising techniques for preparing nano ferrites in bulk scale with great homo geneous particles, the co- precipitation methods with constant P^H has been widely used because of the high crystallinity , homo geneity and good textural properties of the materials produce[24]. The sol gel technique has become very popular recently for the preparation of various mixed metal oxides due to high chemical homo geneity, low processing temperature and the possibility of controlling the size and morphology of particles

The Ni-Zn ferrite is a spinal with crystalline structure belonging to cubic system having large number of application due to its high value of magnetic permeability, high electrical resistivity, high Curie temperature and low power loss and high frequencies[25-27]. Ni-Zn ferrite with various composition have great application in microelectronics, magneto optics and as a micro wave device component[28-30].It is a known fact that particle size and morphology of the nano particles may be controlled by the reaction condition. In the present study Ni-Zn ferrite nano particles are prepared through co-precipitation and sol gel methods and a comparison is made by studying their structural properties .The obtained nano particles are characterized by different techniques such as X-ray diffraction, Thermal analysis, Transmission Electron Microscope and Scanning electron microscopy.

EXPERIMENTAL

Synthesis of Ni-Zn ferrite by Co-precipitation method

$Ni_{1-x}Zn_xFe_2O_4$ spinel ferrite nanocrystalline samples were prepared by co-precipitation method as follows. A mixed solution of stoichiometric amounts of $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $Fe(NO_3)_3$ was prepared. This mixed solution was added drop wise from a burette into an NH_4OH solution, maintaining the pH at ~8. The pH of the solution was kept constant by adding dilute NH_4OH from another burette. The resultant mixture was boiled at 353K for 30 minutes and then allowed to settle. The precipitate was filtered, washed with de-ionized water several times and then dried in vacuum (0.05 Torr) at room temperature. The dried precipitate was then sintered at temperature 773K for 2 hrs.

Synthesis of Ni-Zn ferrite by Sol-gel method

$Ni_{1-x}Zn_xFe_2O_4$ spinel ferrite nanocrystalline samples were prepared by Sol-gel method as follows. Stoichiometric amount of Ferric nitrate Zinc nitrate and Nickel nitrate was dissolved in deionised water and mixed with an aqueous solution of citric acid in 1:1 molar ratio of cation to citric acid. To this solution ammonia solution is added until a clear solution was obtained. The resulting homogeneous solution was refluxed at 353K for 1 hour and then kept in the oven at 373K for 2 hours. A viscous liquid gel was formed which was dried at 473K in the oven. During drying, the gel became a fluffy mass, which was heated for 2 hrs at 773K.

Instruments and analysis

X-ray diffraction analyses of the sample was carried out with a Bruker diffraction unit (model PM 1710) using CoK_α (λ=1.79 Å) radiation with a Ni filter. The d_{hkl} values corresponding to the $2\theta_{hkl}$ values obtained from diffractograms were calculated from Bragg's equation $n\lambda = 2\, d_{hkl} \mathrm{Sin}\theta_{hkl}$ and compared with JCPDS data file. The crystallite size of the nanocrystalline samples were determined from X-ray line broadening analyses applying Scherrer formula, considering the half width ($\beta_{1/2}$) of the peak with highest intensity .The lattice parameter a of the ferrite samples were determined by the equation $1/d^2=1/a^2(h^2+k^2+l^2)$

Thermal analysis of all the $Ni_{1-x}Zn_xFe_2O_4$ precursor samples (x=0.2, 0.4, 0.6, and 0.8) were carried out with a Thermal Analyzer (Perkin Elmer Pyris Diamond TG-DTA) in the temperature region 303K-973K in air by recording DTA and TG curves. A linear rate of heating of 10^0C/min. was maintained during all the measurements.

Microstructural analyses were carried out using a transmission electron microscope (TEM) (Model JEM 2100F) operating at a voltage of 200KV and scanning electron microscope (SEM) (Model ZEISS EVO 60) Operating at a maximum acceleration voltage of 30KV .The samples for

TEM measurements were prepared from a suspension of finely powdered samples in absolute alcohol. An optimum ratio of alcohol to the powdered samples was maintained to get a slightly turbid suspension. The suspension was agitated in an ultrasonic bath to avoid agglomeration of the particles. A drop of the suspension was carefully placed on a carbon coated copper grid, dried for half an hour in air, and then loaded into the microscope for analyses.

RESULT AND DISCUSSION

The XRD patterns in Fig.1 A show that all the $Ni_{1-x}Zn_xFe_2O_4$ (x=0.2, 0.4, 0.6 and 0.8) samples prepared by Co-precipitation method and, Fig.1 B for $Ni_{1-x}Zn_xFe_2O_4$ (x=0.2, 0.4, 0.6 and 0.8) samples prepared by Sol-gel method sintered at temperatures 773K are single phase spinel oxides. The figure however, show that the lines in the XRD patterns of samples sintered at 773 K, are not very sharp as is expected for nanocrystalline samples. The average crystallite size of these samples prepared by Co-precipitation method were found to be in the range of 12nm to 15 nm where as the range is 17 nm to 28 nm for sample prepared by Sol-gel method. Their lattice parameter and crystallite size values of these samples are shown in Table 1 A and B. It is observed that the lattice parameter a increases linearly with increase in zinc content as shown in table 1. The reason for this increase of lattice parameter values may be due to the larger ionic radii of Zn^{+2} (88 pm) as compared to Ni^{+2} (83 pm). These results indicate that the $Ni_{1-x}Zn_xFe_2O_4$ (x=0.2, 0.4, 0.6 and 0.8) samples nanocrystalline samples prepared by co-precipitation and Sol-gel method followed by sintering at 773 K are nanocrystalline spinel ferrites. Although in the X-ray diffraction peaks of the samples prepared by Co-precipitation method are broadened and their intensity is weaker than that of sample prepared by Sol-gel method.

Table 1A: Chemical composition, sintering temperature, lattice parameter and crystallite size of $Ni_{1-x}Zn_xFe_2O_4$ samples by co-precipitation method.

$Ni_{1-x}Zn_xFe_2O_4$	Sintering temperature(K)	LatticeParameter (Å)	Crystallite size (nm)
X=0.8	773	8.42	14.69
X=0.6	773	8.38	12.57
X=0.4	773	8.34	12.30
X=0.2	773	8.30	12.07

Table 1B: Chemical composition, sintering temperature, lattice parameter and crystallite size of $Ni_{1-x}Zn_xFe_2O_4$ samples prepared by sol-gel method.

$Ni_{1-x}Zn_xFe_2O_4$	Sintering temperature(K)	Lattice Parameter (Å)	Crystallite size (nm)
X=0.8	773	8.41	28.43
X=0.6	773	8.37	19.45
X=0.4	773	8.33	17.45
X=0.2	773	8.30	18.26

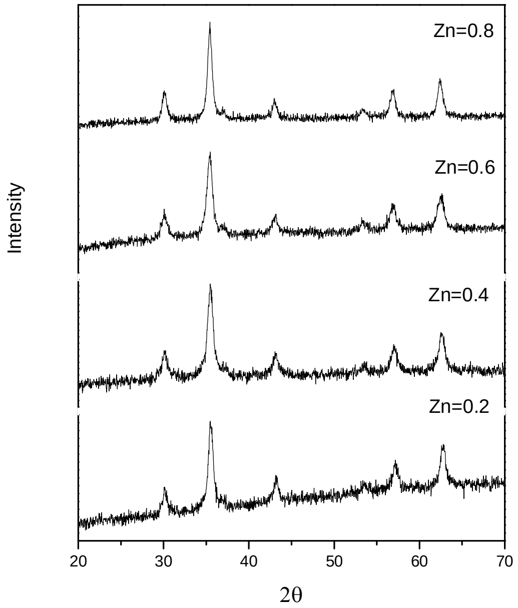


Fig. 1 A. XRD patterns of $Ni_{1-x}Zn_xFe_2O_4$ samples nanocrystalline samples prepared by co-precipitation method

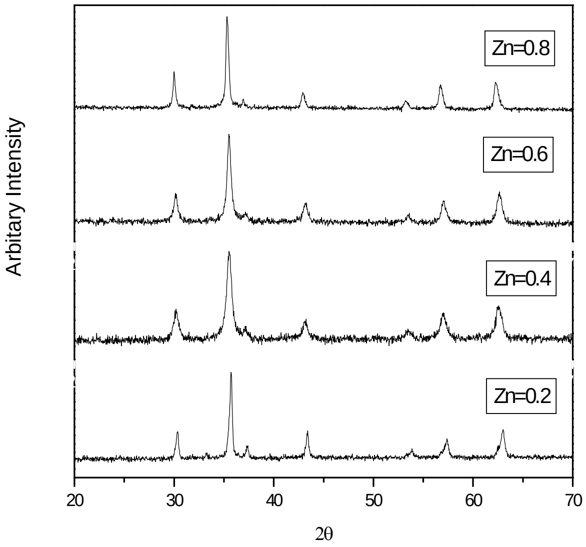


Fig. 1 B. XRD patterns of $Ni_{1-x}Zn_xFe_2O_4$ samples nanocrystalline samples prepared by Sol-gel method

Fig 2 A shows the thermograms (DTA and TG curves) of the $Ni_{1-x}Zn_xFe_2O_4$ precursor sample prepared by Co-precipitation method in the temperature region 303K to 923K. DTA curve shows the presence of one endothermic(373K) and one exothermic peak (423K) and TG curve shows that both the DTA peaks are accompanied with weight loss. The first endothermic peaks appear to be due to loss of adsorbed surface water. On further heating, appearance of an exothermic peak in the DTA plot, accompanied with large weight loss in TG is probably due to decomposition of the metal hydroxide and formation of Nickel Zinc ferrite. Formation of the ferrite in the temperature at 573K is confirmed from the XRD patterns of the samples. The small continuous weight loss in TG above 773K appears to be due to loss of the tightly bound water (grain boundary water) present in the sample[31].

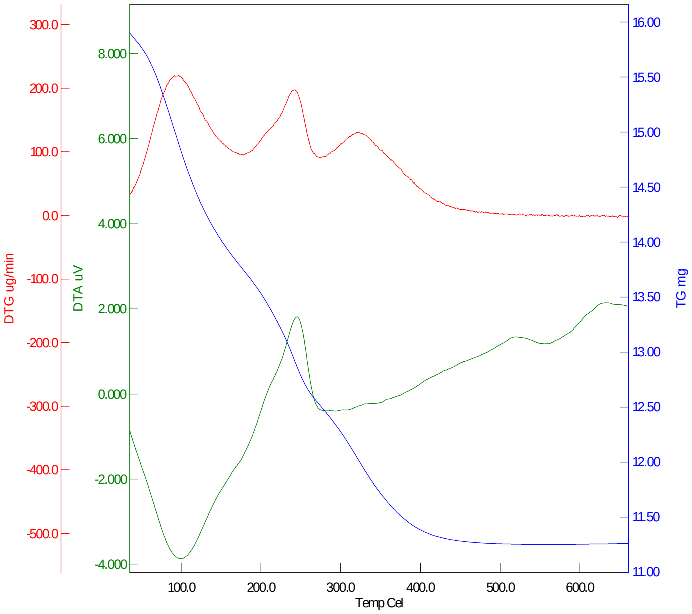


Fig. 2 A. DTA and TG curves of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ Precursor sample prepared by co-precipitation Method

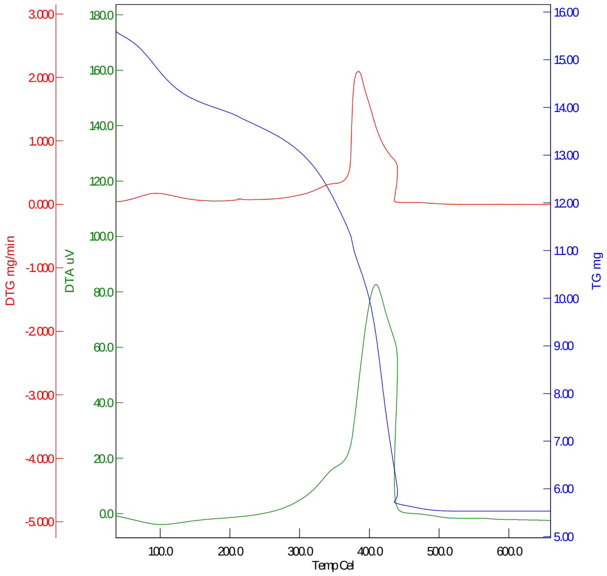
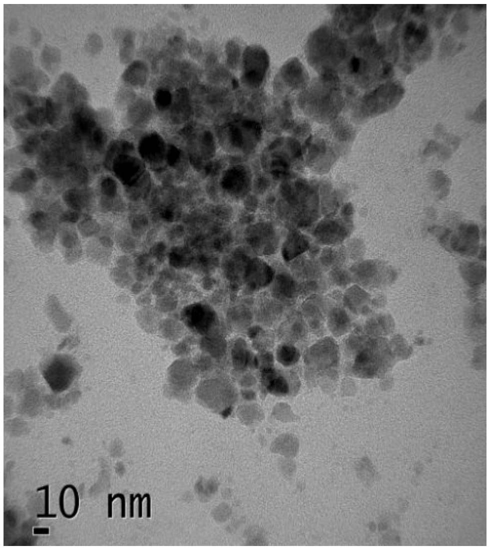


Fig. 2 B. DTA and TG curves of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ prepared by Sol-Gel method

The DTA/TG curve of citrate precursor fluffy mass are shown in Fig 2 B. In Fig. 2 B DTA curve shows the presence of one exothermic peaks with large weight loss in TG is probably due to decomposition of metal citrate precursor due to formation and crystallization of the ferrite phase, which is complete by 723K. Formation of the ferrite around this temperature is confirmed by XRD data.

Figure3A and 3B indicates the TEM micrographs of the $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Ni_{0.2}Zn_{0.8}Fe_2O_4$ samples prepared by the Co-precipitation method, having a considerably large surface area. The particle sizes of these samples are 23nm and 26 nm respectively derived TEM micrographs. Figure 3C indicate the TEM micrographs of the $Ni_{0.4}Zn_{0.6}Fe_2O_4$ sample prepared by the Sol-gel method, having particle size 35nm derived TEM micrographs. The particle size derived from TEM micrographs is greater than the crystallite size estimated from the XRD data. This is indicative of the fact that every particle is formed by the aggregation of a large number of crystallites or grains.



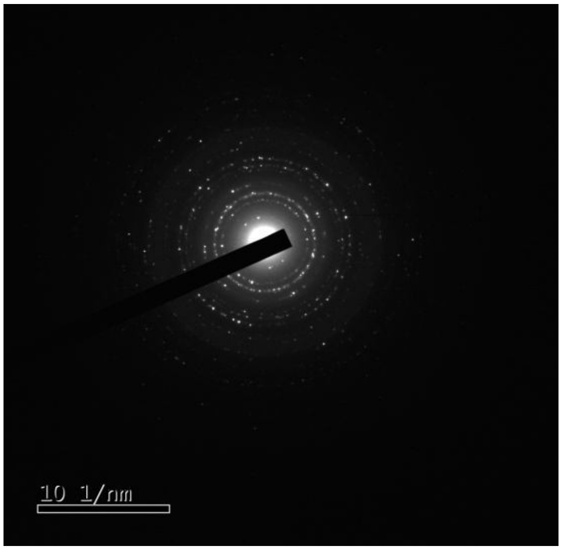


Fig.3A: TEM of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ prepared by co-precipitation method

Fig. 4A: SAED patter of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ prepared by co-precipitation method

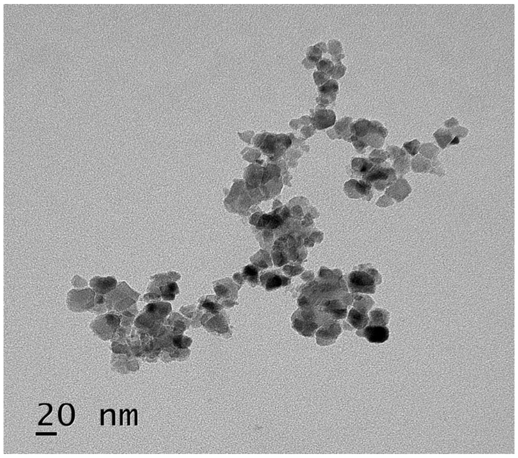


Fig. 3B: TEM of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ prepared by co-precipitation method

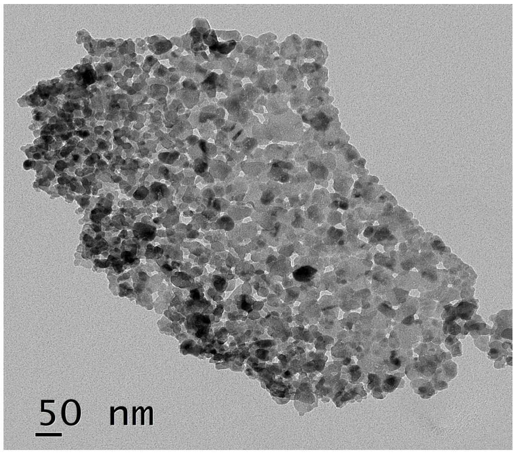


Fig. 3C: TEM of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ prepared by sol-gel method

The selected-area electron diffraction (SAED) pattern of the Nickel zinc ferrite is shown in figure 4A. The ED pattern consists of concentric rings with spots over the rings. This feature indicates the samples are crystalline in nature[32-33]. Most important thing is that the nanoparticles synthesized by sol-gel are more crystalline as compared to co-precipitated particles. This may be attributed to that in co-precipitation we used constant P^H during preparation which controlled the size and agglomeration of particles. However, in sol-gel method uncontrolled agglomeration and layer thickness of citrate gel may lead to large particles[24].

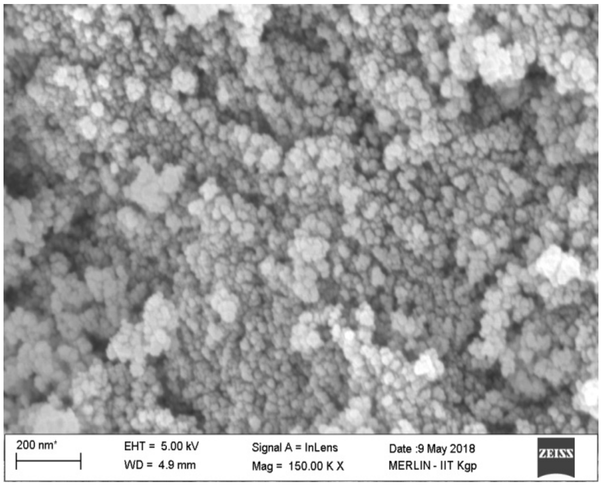


Fig.5A: SEM of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ prepared by co-precipitation method

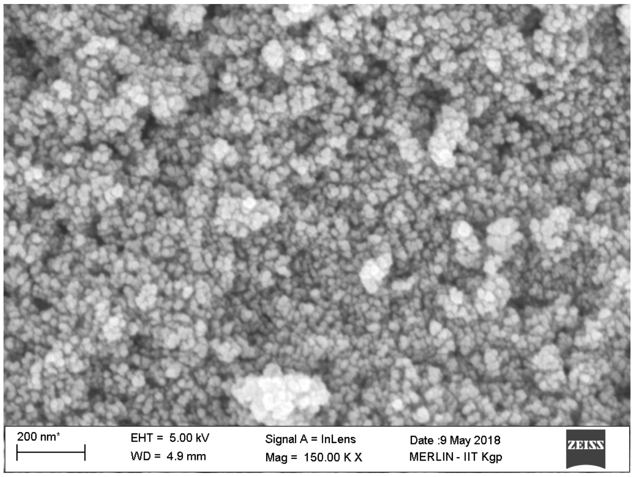


Fig.5C: SEM of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ prepared by co-precipitation method

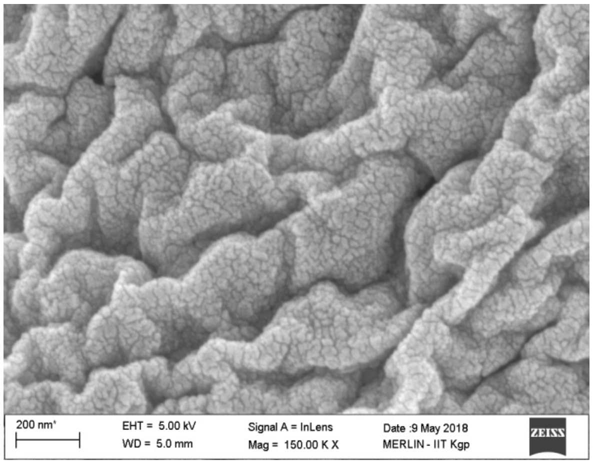


Fig.5B: SEM of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ prepared by sol-gel method

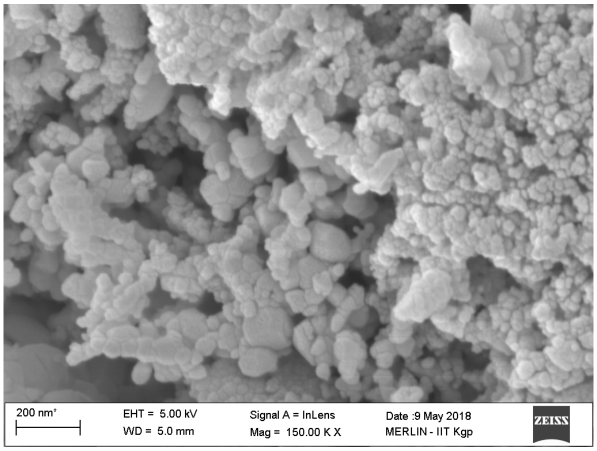


Fig.5D: SEM of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ prepared by sol-gel method

The SEM photograph of Ni-Zn ferrite samples (figure 5 A & B) reveals that sample exhibit a compact arrangement of homogeneous nano particles with roughly spherical shape.

CONCLUSION

From these results it may be concluded that $Ni_{1-x}Zn_xFe_2O_4$ (x=0.2, 0.4, 0.6 and 0.8) samples prepared by sol-gel method are more crystalline and have larger particle size than the samples prepared by co-precipitation method. TEM micrographs of Ni-Zn ferrite samples prepared by sol-gel method have large particle size due to uncontrolled agglomeration and layer thickness of citrate gel, where as the samples prepared by co-precipitation method have small particle size and less agglomeration.

ACKNOWLEDGEMENTS

The author wishes to thank University Grants Commission (UGC- ERO), Minor Research Project, for financial assistance.

REFERENCES

1. Xu Q, Wei Y, Liu Y, Ji X, Yang L, Gu M. Preparation of Mg/Fe spinel ferrite nanoparticles from Mg/Fe-LDH microcrystallites under mild conditions. Solid State Sci .2009; 11(2): 472-478.
2. Tian MB. Magnetic Material Beijing. Tsinghua University Press; 2001
3. Pena MA, Fierro JLG. Chemical Structures and Performance of Perovskite Oxides. Chem Rev. 2001; 101(7): 1981-2018.
4. Ajayan PM, Redlich P, Ru"hle M. Structure of carbon nanotube-based nanocomposites. J Microscopy. 1997; 185(2): 275-282.
5. Baykal A, Kasapoglun, Durmus Z, Kavas H, Toprak MS, Koseoglu Y. CTAB Assisted Hydrothermal Synthesis and Magnetic Characterization of $Ni_xCo_{1-x}Fe_2O_4$ Nanoparticles (x = 0.0, 0.6, 1.0).Turkish Journal of Chemistry .2009; 33: 33-45.
6. Gunjakar JL, More AM, Gurav KV, Lokhande CD. Chemical synthesis of spinel nickel ferrite ($NiFe_2O_4$) nano- sheets. Appl Surf Sci. 2008; 254(18): 5844-5848
7. Borg R.J. and G.D. Dienes. Physical Chemistry of Solids (Academic san Diego, CA). 1992
8. Mahmoudi M, Sant S, Wang B, Laurent S, Sen T. Superparamagnetic iron oxide nanoparticles (SPIONs): development, surface modification and applications in chemotherapy. Advanced Drug Delivery Reviews. 2010; 63: 24-46
9. H.B. Na, I.C. Song, T. Hyeon, Inorganic nanoparticles for MRI contrast agents, Advanced Materials. 2009; 21: 2133–2148.
10. Gubbala S, Nathani H, Koizol K, Misra R D K . Magnetic properties of nanocrystalline Ni-Zn, Zn-Mn, Ni-Mn ferrites synthesized by reverse micelle technique. J. Phys. B. 2004; 348: 317–328.
11. Saafan S A, Meaz T M, El-Ghazzawy E H, El Nimr M K, Ayad M M, Bakr M, A.C. and D.C. conductivity of NiZn ferrite nanoparticles in wet and dry conditions. J. Magn. Magn. Mater. 2010; 322: 2369–2374.
12. Singhal S, Chandra K. Cation distribution and magnetic properties in chromium-substituted nickel ferrites prepared using aerosol route. J. Solid. State. Chem. 2007; 180: 296–300.

13. Singhal S, Namgyal T, Bansal S, Chandra K. Effect of Zn Substitution on the Magnetic Properties of Cobalt Ferrite Nano Particles Prepared Via Sol-Gel Route. J. Electromagnetic Analysis & Applications. 2010; 2: 376-381
14. Snelling E.C. Ferrites for Inductors and Transformers. Research Studies Press, New York, 1983
15. Costa A.C.F.M., Tortella, E., Morelli, M.R., Kiminami, R.H.G.A. Synthesis, microstructure and magnetic propertiesof Ni–Zn ferrites. J. Magn. Magn. Mater. 2003; 256M: 174–182
16. Albuquerque A S, Ardisson, J D, Macedo, W A A . A study of nanocrystalline NiZn–ferrite–SiO_2 synthesized by sol–gel. J. Magn. Magn. Mater. 1999; 192: 277–280
17. Kim YI, Kim D, Lee CS. Synthesis and characterization of $CoFe_2O_4$ magnetic nanoparticles prepared by temperature-controlled co-precipitation method. Physica B (Amestherdam, Neth). 2003; 337(1-4): 42-51.
18. Huo J, Wei M. Characterization and magnetic properties of nanocrystalline nickel ferrite synthesized by hydrothermal method. Material. Letters. 2009; 63: 1183–1184
19. Baykal Al, Kasapoglu N, Koseoglu Y K, Toprak M S, Bayrakdar H. CTAB-assisted hydrothermal synthesis of NiFe2O4 and its magnetic characterization. J Alloys Compd .2008; 464 (1-2):514-518.
20. Hochepied J F, Bonville P, Pileni M P. Nonstoichiometric Zinc Ferrite Nanocrystals: Syntheses and Unusual Magnetic Properties. J Phys Chem. 2000;B 104(5):905-912.
21. Kurian Manju, Divya S. Nair. Effect of preparation conditions on Nickel Zinc Ferrite nanoparticles: A comparison between sol–gel auto combustion and co-precipitation methods. Journal of Saudi Chemical Society. 2013; 20: S517-S522.
22. Vuk Uskokovic, Miha Drofenik, Irena Ban. The Characterisation of nanosized nickel-zinc ferrites synthesis within reverse micelles of CTAB/1-hexanol/water microemulsion, Journal of Magnetism and Magnetic Materials. 2004; 284: 294-302
23. P M Prithviraj Swamy etal. Synthesis and Characterisation Zinc ferrite nanoparticles obtained by self-propagating low temperature combustion method. Bulletin of Materials Science. 2011; 34(7): 1325-1330
24. Chand Mahesh, Kumar A, Pant R P etal. Investigation on $Mn_xZn_{1-x}Fe_2O_4$ (0.1,0.3 and 0.5) nanoparticles synthesized bysol-gel and co-precipitation method, Indian Journal of Engineering & Materials Sciences. 2011;18: 385-389
25. Goldman, A. Modern Ferrite Technology. Van Nostrand Reinhold, New York :1990
26. Gheisari K , Bhame S D, Oh J T,· Javadpour S. Comparative Studies on the Structure and Magnetic Properties of Ni–Zn Ferrite Powders Prepared by Glycine-Nitrate Auto-combustion

Process and Solid State Reaction Method. J Superconductivity and Novel Magnetism. 2013; 26:477–483

27. Harris, V.G. Modern microwave ferrites. IEEE Trans. Magn. 2012; 48(3): 1075–1104
28. Bhattacharjee K, Ghosh C K, Mitra M.K, Das G C, Mukherjee, S. Novel synthesis of $Ni_xZn_{1-x}Fe_2O_4$ ($0 \le x \le 1$) nanoparticles and their dielectric properties. J. Nanopart. Res. 2011; 13: 739
29. Thakur, S, Katyal, S C, Gupta, A, Reddy, V R, Sharma, S K Knobel, M Singh. Nickel-zinc ferrite from reverse micelle process: Structural and magnetic properties, Mossbauer spectroscopy Characterisation. J. Phys. Chem. 2009.; 113: 20785-20794
30. Shobana M K, Sankar S. Characterisation of sol-gel prepared nanoferrites. J. Magn. Magn. Mater. 2009; 321: 599-601
31. Dey S. and Ghose J. Synthesis, characterization and magnetic studies on nanocrystalline $Co_{0.2}Zn_{0.8}Fe_2O_4$, Materials Research Bulletin. 2003; 38: 1653-1660.
32. Wang Q, Yang H, Shi Jiunlin and Zou Guangtian. One drop synthesis of the nanometer particles of γ- Fe_2O_3 by wire electrical explosion method. Materials Research Bulletin. 2001; 36: 503-509
33. Pawaskar N R, Sathaye S D, Bhadbhade M M and Patil K R. Application of liquid-liquid interface reaction technique for the preparation of zinc sulfide nano particulate thin flims. Materials Research Bulletin. 2002; 37: 1539-1546