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Preparation and Characterization of $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$: A New Precursor to $Co_{0.8}Zn_{0.2}Fe_2O_4$ Nanoparticles

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Co – Zn ferrite nanoparticles have been synthesized using carboxylate- hydrazine precursor via thermal decomposition route. The prepared precursor $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$ was characterized by hydrazine, metal analyses, infrared spectral and thermal analyses. Using appropriate annealing conditions, $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles of average size 13 nm were synthesized by thermal treatment of the precursor. The nanoparticles were characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM) and Selected Area Electron Diffraction (SAED) techniques. The details of synthesis and characterization of the nanoparticles are reported in this paper.

Keywords: ferrite nanoparticles, IR, TGDTA, XRD, HRTEM.

1. INTRODUCTION

During the last few decades, nanomaterials constitute an intensively studied class of materials; it is eminent that materials in the realm of nanometer scale show unexpected behaviour with respect to its physical and chemical properties. Nanosized particles are used for magnetic resonance imaging (MRI) and magnetic fluid hyperthermia (MFH) [1]. Magnetic nanoparticles are of great technological importance because of their use in magnetic fluid, information storage system, medical diagnostics, etc. All properties are sensitive to their composition, microstructure and processing conditions. These properties make it a promising material for high density magnetic storage. Commercially, the chemically homogeneous, fine grain size and high density ferrites are important for technological applications. So, the preparation and characterization of the nano-crystalline ferrite powder have gained more attention recently. However, with the development of science and technology, the Co – Zn ferrites have to become higher performance and smaller size. Many methods have been used to synthesize Co – Zn ferrites such as, high-energy ball milling, co-precipitaion or co-deposition, sol–gel, hydrothermal synthesis method, microemulsion technique [2 – 5]. Among the current methods for synthesis of cobalt ferrite, the combustion reaction stands out as an alternative and highly promising method for the synthesis of these ferrites. There has been considerable interest among researchers in the study of hydrazine derivatives of metal carboxylates since they serve as precursors to fine particle oxide materials.

The chemistry of hydrazine is interesting with respect to its ability to form complexes with transition metals.

Hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes [6, 7].

Recently many such thermal decomposition methods are employed for the synthesis of metal and mixed metal oxides using metal carboxylate and carboxylato-hydrazinates complexes of oxalate [8], formate [9], acetate and propionate [10] malonate, succinate and itaconates [11, 12], maleate and tartrate [13, 14] malate [15] and fumarate [16 – 18] have been studied. Among the large number of techniques employed for the synthesis of oxides, thermal treatment is found to be unique and highly versatile. It is an easy and fast process which yields high-purity, homogenous, crystalline oxides in a short time and with less energy. In this paper, we report a novel method of synthesis of Co – Zn ferrites using the inorganic precursor $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$ and detailed structural characterization of these particles.

2. EXPERIMENTAL

Phenylacetic acid (0.9 g, 0.006 mol) was added to 100 ml of distilled water containing 99 – 100 % pure hydrazine hydrate (1.6 ml, 0.03 mol). The solution was heated over water bath to get a clear solution. Then to this clear solution, the metal salt solution containing ferrous sulphate (1.11 g, 0.004 mol), cobalt nitrate hexahydtrate (0.86 g, 0.003 mol) and zinc nitrate hexahydrate (0.2 g, 0.0007 mol) was added with constant stirring. The yellow coloured compound precipitated slowly, was kept for some time, filtered, washed with distilled water and alcohol followed by diethylether and then air dried.

$Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$ thus prepared was taken in a clean silica crucible and heated gently at the starting and strongly when the decomposition starts. As a result the precursor was completely decomposed to ferrite $Co_{0.8}Zn_{0.2}Fe_2O_4$.

3. CHARACTERIZATION

All the chemicals used were pure commercial grade. The hydrazine content in the precursor was determined by volumetric analysis using (0.25M) KIO_3 as the titrant

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under Andrews' condition [19]. The percentage of cobalt, zinc and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [19]. The metal content in the sintered oxide sample were also determined by EDX.

Infrared analysis of the precursor $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$ was carried out on a Perkin-Elmer model 597 spectrophotometer using KBr pellets. The thermal measurements (TG- DSC) are performed using a Netzsch SDT Q600 device from RT to 1000°C in nitrogen atmosphere. The crystalline phases are identified by XRD powder methods using a Seifert X-ray diffractometer (CuK_radiation). The morphology of the as synthesised nano particle was determined by a Scanning Electron Microscope (SEM, Philips XL-30) which is equipped with an Energy-Dispersive X-ray spectrometer (EDX). High Resolution Transmission Electron Microscopy (HR-TEM) images and Select Area Electron Diffraction Pattern (SAED) were collected using a Jeol Jem 2100 advanced analytical electron microscope to determine the shape and size of the nanoparticles.

4. RESULTS AND DISCUSSION

The observed percentage of hydrazine (14.46), cobalt (19.47), zinc (5.32) and iron (47.42) are very well in agreement with the calculated values of 14.22, 19.98, 5.32 and 47.34. From the above data the chemical formula for the precursor is tentatively assigned as $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$.

The infra-red spectrum of the precursor shows a band in the range 3295 cm^{-1} due to N- H stretching frequency and in the range of 1534 cm^{-1} due to NH_2 deformation. The separation of asymmetric and symmetric ($\upsilon_{asymm} - \upsilon_{sym}$) carboxylate stretching of 221 cm^{-1} indicates the unidentate coordination [20, 21] of carboxylate ions. The N-N stretching frequency of hydrazine moieties were observed at 977 cm^{-1} indicating their bidentate bridging nature [22]. This IR data thus reveals that the cobalt zinc ferrous phenylacetate hydrazinate is formed.

Table 1. Thermal decomposition data

Compound	Thermogravimetry (TG)		Decomposition product
	Temp. range, °C	Mass loss, %	
$Co_{0.8}Zn_{0.2}Fe_2$ $(PhAc)_3((N_2H_4)$	RT- 95	4	$Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3$ $(N_2H_4)_2$
	95-168	11	$Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3$
	168-323	41	$Co_{0.8}Zn_{0.2}Fe_2(Ph)O_2$
	323-512	65	$Co_{0.8}Zn_{0.2}Fe_2O_4$

The cobalt zinc ferrous precursor shows multistep decomposition in nitrogen atmosphere (Fig. 1). Initially it loses one hydrazine molecule in the temperature range from room temperature to 95 °C and in the temperature range 95 – 168 °C it eliminated two hydrazine molecules. Both these stages are exothermic at 77 and 168 °C. TG curve from 168 – 456 °C is due to the decarboxylation of the dehydrazinated precursor. DTA curve shows exothermic peak in this region with the peak temperature of 438 °C due to decarboxylation. $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$ precursor loss thermo gravimetrically from room temperature to 700 °C to yield $Co_{0.8}Zn_{0.2}Fe_2O_4$ (Table 1) as the final product.

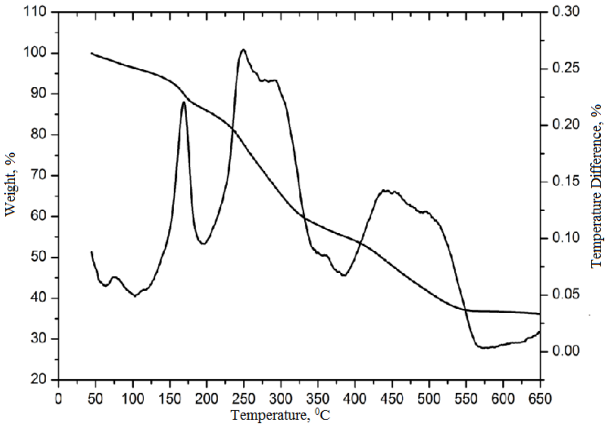


Fig. 1. TG-DTA of $Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$

The phase and its purity were confirmed by powder X-ray diffraction (XRD). The formation of monophasic $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles soon after the thermal decomposition of the precursor has been confirmed by XRD. Fig. 2 shows the peak position and the relative intensity of all the diffraction peaks are well matched with standard powder diffraction data and no impurity peak was observed, which indicated the high purity crystalline $Co_{0.8}Zn_{0.2}Fe_2O_4$ was synthesised. The more intense peak (311) confirms the formation of single-phase cubic spinel structure. The broadening nature of the XRD peaks indicates that the crystallite size of the as-prepared sample is within nanometer scale. Considering the more intense peak, the average crystallite sizes are calculated by Scherrer formula [24, 25].

$$D = (0.94\lambda)/B\cos(\theta), \quad (1)$$

where, λ is the wave length of X-rays, B is the full width at half maximum, θ is the diffraction angle. The Scherrer formula analysis showed that the average diameter of the grain sizes of $Co_{0.8}Zn_{0.2}Fe_2O_4$ is 13 nm.

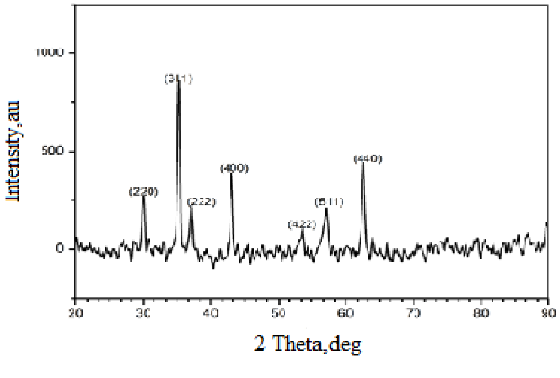
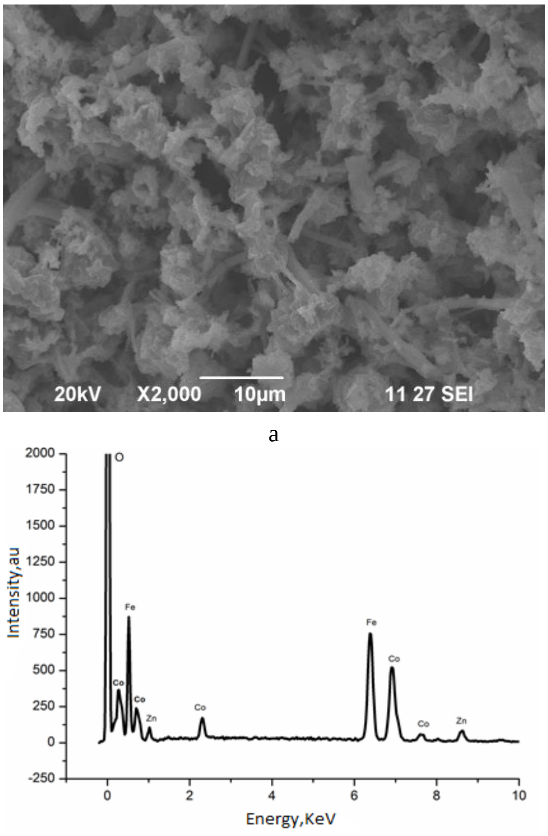


Fig. 2. XRD of $Co_{0.8}Zn_{0.2}Fe_2O_4$

The microstructure plays an important role in realizing many application-oriented ferrite properties. The Fig. 3 a at higher magnification provides immense evidence that $Co_{0.8}Zn_{0.2}Fe_2O_4$ has nano rod like agglomerated morphology consists of nanosized particles with a narrow distribution.

In order to confirm the chemical composition, EDX analysis was carried out and is shown in Fig. 3 b. This compositional analysis method results comply with what is expected from the synthesis. The result from EDX spectra shows that as-prepared $Co_{0.8}Zn_{0.2}Fe_2O_4$ particles contain Co, Zn, Fe and O, and no contamination element was detected, indicating that the chemical formula of the as-prepared samples is consistent with the experimental stoichiometric.



a

b

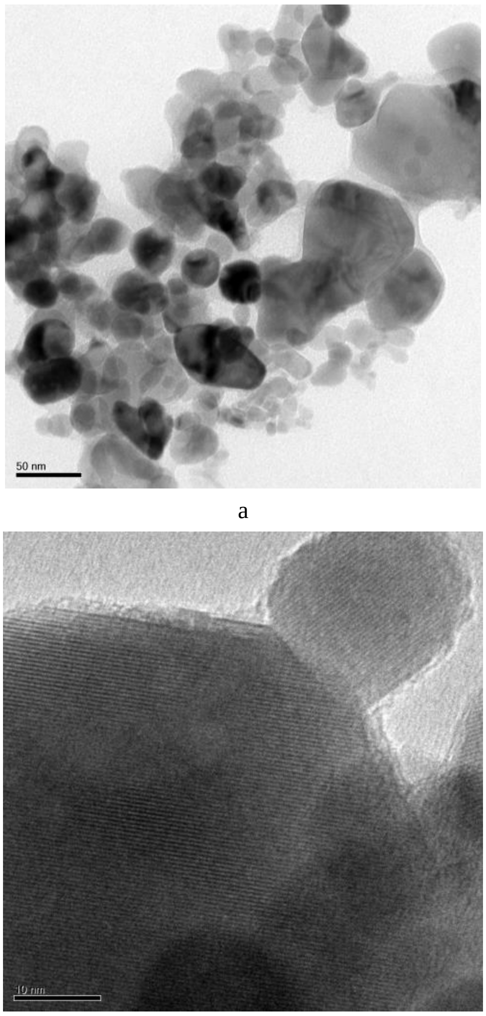
Fig. 3. a – SEM image of $Co_{0.8}Zn_{0.2}Fe_2O_4$; b – SEM-EDX of $Co_{0.8}Zn_{0.2}Fe_2O_4$

The size and morphology of the as-produced sample in detail were investigated by HRTEM. High Resolution Transmission Electron Microscopy (HRTEM) images (Fig. 4 a and b) of the obtained nano particles shows that Co – Zn ferrite was almost spherical ultrafine nanoparticles, homogenously dispersed with agglomeration. From the Fig. 4b the crystallographic orientation of the $Co_{0.2}Zn_{0.8}Fe_2O_4$ was investigated by HRTEM. The $Co_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles were clearly observed. The particle size calculated by HRTEM micrography was in the range of 11 – 15 nm, which is in agreement with that calculated using the Debye-Scherrer formula.

The electron diffraction pattern from the HRTEM image (Fig. 5) shows multiple diffraction rings, indicating crystalline structure formation. A careful analysis of this SAED pattern reveals that besides the diffraction rings of $Co_{0.8}Zn_{0.2}Fe_2O_4$, no additional rings were observed. The bright electron diffraction rings for $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles shows that the $Co_{0.8}Zn_{0.2}Fe_2O_4$ is fine nanocrystalline particles.

5. CONCLUSION

In summary, $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles were synthesised by thermal decomposition of the precursor complex ($Co_{0.8}Zn_{0.2}Fe_2(PhAc)_3(N_2H_4)_3$) at room temperature. From IR Spectra, the separation of asymmetric and symmetric ($\upsilon_{asymm} - \upsilon_{sym}$) carboxylate stretching of 221 cm^{-1} indicates the unidentate coordination of carboxylate ions.



a

b

Fig. 4. HRTEM images of $Co_{0.2}Zn_{0.8}Fe_2O_4$

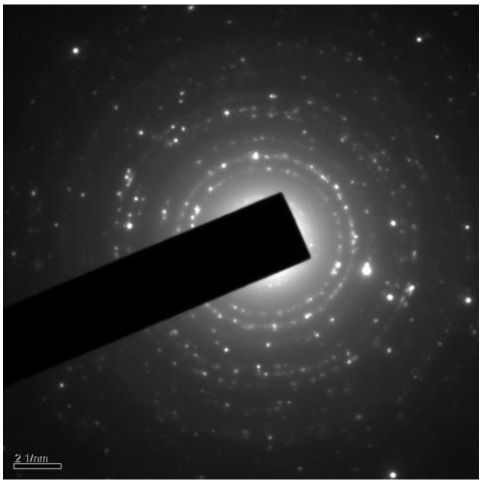


Fig 5. SAED pattern of $Co_{0.8}Zn_{0.2}Fe_2O_4$

The N-N stretching frequency of hydrazine moieties are observed at 977 cm^{-1} indicating their bidentate bridging nature. Thermal studies of the precursor complex shows multi step degradation to form cubic spinal $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles, which is also confirmed by XRD studies.

The average particle size determined by HRTEM is in agreement with that the particle size calculated using the Debye-Scherrer formula.

Thus, this novel route gives an efficient method of preparation of $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles involving low cost, low energy, high purity and high nanocrystallinity.

REFERENCES

1. **de Biasi, R. S., Figueiredo, A. B. S., Fernandes, A. A. R., Larica, C.** Synthesis of Cobalt Ferrite Nanoparticles using Combustion Waves *Solid State Communication* 144 2007: pp. 15 – 17. http://dx.doi.org/10.1016/j.ssc.2007.07.031
2. **Kim, Y. I., Kim, D., Lee, C. S.** Synthesis and Characterization of $CoFe_2O_4$ Magnetic Nanoparticles Prepared by Temperature-Controlled Coprecipitation Method *Physica B: Condensed Matter* 337 2003: pp. 42 – 51. http://dx.doi.org/10.1016/S0921-4526(03)00322-3
3. **Fang, J., Shama, N., Tung, L. D., Young Shin, E., O'Connor, Ch. J., Stokes, K. L., Caruntu, G., Wiley, J. B., Spinu, L., Tang, J.** Ultrafine $NiFe_2O_4$ Powder Fabricated from Reverse Microemulsion Process *Journal of Applied Physics* 93 2003: pp. 7483 – 7485.
4. **Mozaffari, M., Amighian, J.** Preparation of Al-Substituted Ni Ferrite Powders via Mechanochemical Processing *Journal of Magnetism and Magnetic Materials* 260 2003: pp. 244 – 249. http://dx.doi.org/10.1016/S0304-8853(02)01338-0
5. **Gul, I. H., Abbasi, A. Z., Amin, F., Anis-ur-Rehman, M.** Structural, Magnetic and Electrical Properties of $Co_{1-x}Zn_xFe_2O_4$ Synthesized by Co-Precipitation Method *Journal of Magnetism and Magnetic Materials* 311 2007: pp. 494 – 499. http://dx.doi.org/10.1016/j.jmmm.2006.08.005
6. **Porob, R. A., Khan, S. Z., Mojumdar, S. C., Verenker, V. M. S.** Synthesis, TG, DSC and Infrared Spectral Study of $NiMn_2(C_4H_4O_4)_3$_$6N_2H_4$: A Precursor for $NiMn_2O_4$ Nanoparticles *Journal of Thermal Analysis and Calorimetry* 86 2006: pp. 605 – 608. http://dx.doi.org/10.1007/s10973-006-7715-y
7. **More, A., Mojumdar, S. C., Parab, S., Verenker, V. M. S.** Preparation, Purification and Characterisation of Nanoparticle Ferrite from Novel Fumarato–Hydrazinate Precursor *15 th CTAS Annual Workshop and Exhibition.* National Research Council Canada, Bouchervill Quebec J4B 6Y4 Canada 2005: pp. 22 – 25.
8. **Gajapathy, D., Patil, K. C., Pai Vernekar, V. R.** Low Temperature Ferrite Formation using Metal Oxalate Hydrazinate Precursor *Materials Research Bulletin* 17 1982: pp. 29 – 32. http://dx.doi.org/10.1016/0025-5408(82)90179-9
9. **Randhawa, B. S., Kaur, S., Bassi, P. S.** Thermal Decomposition of Strontium and Barium Malonates *Journal of Thermal Analysis and Calorimetry* 55 (3) 1999: pp. 789 – 796. http://dx.doi.org/10.1023/A:1010169414001
10. **Randhawa, B. S., Dosanjh, H. S., Kumar, N.** Synthesis of Potassium Ferrite by Precursor and Combustion Methods A Comparative Study *Journal of Thermal Analysis and Calorimetry* 95 (1) 1999: pp. 75 – 80. http://dx.doi.org/10.1007/s10973-008-8920-7
11. **Sivasankar, B. N.** Cobalt(II), Nickel(II) and Zinc(II) Dicarboxylate Complexes with Hydrazine as Bridged Ligand Characterization and Thermal Degradation *Journal of Thermal Analysis and Calorimetry* 86 (2) 2006: pp. 385 – 392.
12. **Sivasankar, B. N., Govindrajan, S.** Acetate and Malonate Complexes of Cobalt(II), Nickel(II) and Zinc(II) with Hydrazinium Cation: Preparation, Spectral and Thermal Studies *Journal of Thermal Analysis and Calorimetry* 48 (6) 1997: pp. 1401 – 1413. http://dx.doi.org/10.1007/BF01983451
13. **Rane, K. S., Verenkar, V. M. S.** Synthesis of Ferrite Grade c-Fe_2O_3 *Bulletin of Materials Science* 24 (1) 2001: pp. 39 – 45. http://dx.doi.org/10.1007/BF02704838
14. **Randhawa, B. S., Kaur, M.** A Comparative Study on the Thermal Decomposition of Some Transition Metal Maleates and Fumarates *Journal of Thermal Analysis and Calorimetry* 89 (1) 2007: pp. 251 – 255.
15. **Khalil, I., Petit-Ramel, M. M.** Polynuclear Complexes Quantitative and Qualitative Study of Copper-Yttrium Malate and Copper-Uranyl Malate *Journal of Inorganic and Nuclear Chemistry* 41 (5) 1979: pp. 711 – 716. http://dx.doi.org/10.1016/0022-1902(79)80359-0
16. **Gawas, U. B., Mojumdar, S. C., Verenkar, V. M. S.** $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2(C_4H_2O_4)_3$_$6N_2H_4$ Precursor $Ni_{0.5}Mn_{0.1}Zn_{0.4}Fe_2O_4$ Nanoparticles Preparation, IR Spectral, XRD, SEM-EDS and Thermal Analysis *Journal of Thermal Analysis and Calorimetry* 96 (1) 2009: pp. 49 – 52. http://dx.doi.org/10.1007/s10973-008-9836-y
17. **Gonsalves, L. R., Verenkar, V. M. S., Mojumdar, S. C.** Preparation and Characterization of $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_36N_2H_4$: a Precursor to Prepare $Co_{0.5}Zn_{0.5}Fe_2O_4$ Nanoparticles *Journal of Thermal Analysis and Calorimetry* 96 (1) 2009: pp. 53 – 57. http://dx.doi.org/10.1007/s10973-008-9837-x
18. **More, A., Verenkar, V. M. S., Mojumdar, S. C.** Nickel Ferrite Nanoparticles Synthesis from Novel Fumarato-Hydrazinate Precursor *Journal of Thermal Analysis and Calorimetry* 94 (1) 2008: pp. 63 – 67. http://dx.doi.org/10.1007/s10973-008-9189-6
19. **Vogel, I.** A Text Book of Quantitative Inorganic Analysis 4th Ed *Longman* London 1986.
20. **Nakamoto, K.** Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B 6th ed. New York, John Wiley, 1978.
21. **Sawant, S. Y., Verenkar, V. M. S., Mojumdar, S. C.** Preparation, Thermal, XRD, Chemical and FTIR Spectral Analysis of $NiMn_2O_4$ Nanoparticles and Respective Precursor *Journal of Thermal Analysis and Calorimetry* 90 (3) 2007: pp. 669 – 672.
22. **Braibanti, A., Dallavalle, F., Pellinghelli, M. A., Leporati, E.** The Nitrogen-Nitrogen Stretching Band in Hydrazine Derivatives and Complexes *Inorganic Chemistry* 7 (7) 1968: pp.1430 – 1433.
23. **Cullity, B. D.** Elements of X- Ray Diffraction *Addison – Wesley Publishing Company*. JNC, 1967.
24. **Pandit, A. A., More, S. S., Dorik, R. G., Jadhav, K. M.** Structural and Magnetic Properties of $Co_{1+y}Sn_yFe_{2-2y-x}Cr_xO_4$ *Bulletin of Materials Science* 26 (5) 2003: pp. 517 – 521. http://dx.doi.org/10.1007/BF02707350
25. **Akther Hossain, A. K. M., Mahmud, S. T., Seki, M., Kawai, T., Tabata, H.** Structural, Electrical Transport and Magnetic Properties of $Ni_{1-x}Zn_xFe_2O_4$ *Journal of Magnetism and Magnetic Materials* 312 (1) 2007: pp. 210 – 219. http://dx.doi.org/10.1016/j.jmmm.2006.09.030