International Journal for Multidisciplinary Research (IJFMR)
E-ISSN: 2582-2160 ● Website: www.ijfmr.com ● Email: editor@ijfmr.com

Synthesis of Iron Oxide Nanomaterials with Ferrous Sulphate/Ferric Chloride Precursor at Different Reaction Conditions, and Studied the Structural, Morphology, Optical and Magnetic Properties

Dr. P. Laveena Manjulatha

Assistant Professor of Physics, Department of Physics
MVS Government Degree College (A), Mahabubnagar -509001,
E-mail:laveenamanjulatha@gmail.com

Abstract

Iron oxide nanoparticles were synthesized with Fe+2 and Fe+3 precursors in a 1: 2 ratio by using the hydrothermal method under different reaction temperatures and alkaline conditions. The iron oxide nanoparticles were characterized for structure, morphology, optical and magnetic properties. X-ray diffraction analysis confirmed that the samples prepared at different hydrothermal temperatures exhibited a magnetite structure, the increased intensity of the peaks indicates a high degree of crystallinity. The transformation of goethite to Fe3O4 structure was observed with variation of the pH value. The morphological study revealed that some samples exhibited spherical particles and some others exhibited a mixed morphology of spheres and rods. The iron oxide synthesized at 190 8C exhibited better magnetic properties due to the uniform distribution of spheres with particles size in the range, 18 – 25 nm.

Keywords: Hydrothermal temperature; Alkaline concentration; Magnetite nanoparticles; Saturation magnetization

Introduction

In recent years, the production of iron oxide nanoparticles (IONPs) has gained increasing attention because of their potential applications in magnetic memory devices, magnetic fluids, sensors, catalysis, production of pigments, drug delivery, and removal of heavy metal ions from vast water applications [1 – 4] due to their unique properties such as high surface to volume ratio, quantum confinement, quantization of energy, and random molecular motion. IONPs have also received considerable attention in biomedical applications on account of biocompatibility, high chemical and physical stability, environmental benignity, abundance and inexpensive production [5]. Different physical and chemical techniques such as solid-state chemical reaction [6], co-precipitation [7], sono-chemical [8], micro emulsion [9], thermal decomposition [10], hydrothermal [11, 12], and flame spray pyrolysis [13] have been developed for obtaining a better size and size distribution of IONPs. Although several methods have been adopted for preparing IONPs, many unresolved problems still exist such as preparation of particles with required shape, size, size distribution, and phase formation. For this many researchers have used ferrous and ferric iron salts in a 1: 2 ratio due

to better control over the magnetite phase and lower particle sizes can be obtained. Iida et al. [14] prepared magnetite nanoparticles with different Fe+2 salts alone, and also Fe+2 and Fe+3 mixed salts. This work reported lower particle sizes with the Fe+2 and Fe+3 mixed salts compared to the Fe+2 salt alone. In the present study, we synthesized IONPs using a hydrothermal method at different reaction temperatures and pH conditions. The hydrothermal method facilitates tailoring the particle shape, size, size distribution, and phase formation by adjusting the reaction temperature, reaction time, and pH of the medium. The structural, morphological, optical, and magnetic properties of the synthesized IONPs were studied. The main aim of this study was to assess the effects of the reaction temperature and alkaline concentration (pH) of the medium on the structure, optical and magnetic properties of IONPs to use in biomedical and sensor applications.

2. Experimental Materials and Methods

Details of the materials used and the experimental methods adopted in the present study have been explained Analytical grade ferrous sulfate heptahydrate (FeSO4 · 7H2O), ferric chloride (FeCl3), and sodium hydroxide (NaOH) were purchased from Merck, India. Ethanol was made in china and distilled water was used as a solvent. In the first set of experiments, 0.3 M FeSO4 and 0.6 M FeCl3 solutions were prepared in a 1: 2 ratio by dissolving them in distilled water separately, followed by vigorous stirring of the mixed solution for 30 min to form a homogeneous solution of ferrous and ferric ions. The solution was then titrated with 5 M NaOH solution and vigorously stirred until a pH*10 was obtained. The entire black precipitated solution was transferred to a Teflon-lined stainless steel autoclave placed in the oven at different temperatures (100, 130, 160, and 190 8C) for 18 h and then allowed to cool naturally to room temperature. The resultant black solid products were washed thoroughly with distilled water and ethanol, and dried for 12 h at 80 8C in an oven. For the second set, the same procedure was followed at different alkaline concentrations (pH*6, 8, 10, and 12) at a constant reaction temperature, 130 8C for 18 h. The nature of the crystallinity and phases were studied using a Bruker D8 advance X-ray diffractometer with CuKa (k = 1.5406 Å) radiation source in the 2h range 20 – 808. The morphology of the synthesized materials was analyzed in a field emission scanning electron microscope (FESEM) (SUPRA-55, Carl Zeiss, Germany). Optical spectra were collected using a UV-visible spectrometer (Lab India, UV3092) over a wavelength range of 250 – 800 nm. The room temperature hysteresis behavior was studied using a vibrating sample magnetometer (VSM) (Princeton Micro Mag, AGM 2900) with a maximum field of ±12.5 kOe.

Results and discussion

Materials characterization

X-ray powder diffraction analysis

XRD is a very significant experimental technique to determine the crystal structure of solids, including geometry, lattice constants, identification of unknown materials and orientation of single crystals etc. The unknown crystal structure of the materials can be identified by matching with standard diffraction pattern of the similar with JCPDS data as reference. Fig. 5.1(a–d) shows the XRD patterns of the IONPs prepared with $FeSO_4/FeCl_3$ precursors at different reaction temperatures (100-190 ºC) and at a constant alkali (pH~10) condition.

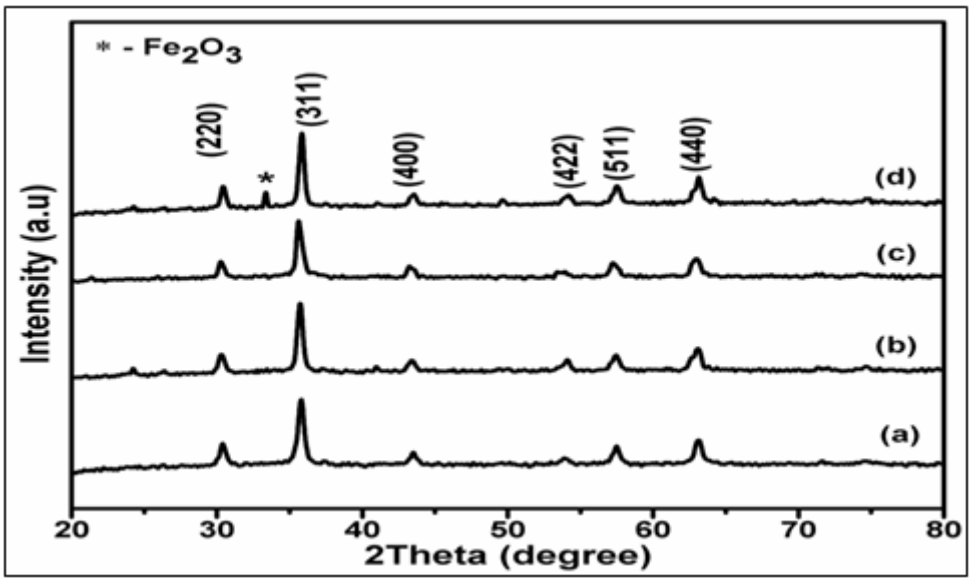

Fig.5.1 XRD patterns of the IONPs synthesized with $FeSO_4/FeCl_3$ at different hydrothermal temperatures (a) 100, (b) 130, (c) 160 and (d) 190 ºC.

All the synthesized materials exhibited Bragg'splanesat 30.4°,35.8°,43.4°,53.9°,57.3°and 63.2° corresponding to (220), (311), (400), (422), (511) and (440) planes, respectively of magnetite (Fe_3O_4) structure. These planes are in accordance with the standard data (JCPDS file no. 79-0417) of spinel cubic structure. The intensity of the peaks increased with an increase of reaction temperature to 160 °C, indicating improvement in crystalline nature. The material prepared at 190 °C showed an extra peak at 33.3°representing Fe_2O_3 due to the effect of higher reaction temperature. This is due to imbalance between the ferrous and ferric ionic ratio. Generally, the ratio between ferrous and ferric ions was 0.5, which gives rise to pure magnetite phase. On other hand extra iron ions leads to Fe_2O_3 [1].

Nevertheless, magnetite and maghemite phases were dubious to differentiate with one another from XRD because of their similar crystalline planes, which require X-ray photoelectron spectroscopy and Mossbauer spectra for accurate phase conformation. However, it was partially done based on color of the synthesized powder and reaction temperature conditions. The previous reports pointed that; the magnetite can be transformed to γ-Fe_2O_3 (maghemite) phase above 250 °C [2]. Fig. 5.2(a-d) shows the XRD pattern of the IONPs prepared at different pH conditions of 6, 8, 10 and 12. The pH 6 and 8 showed a goethite (α-FeOOH) structure (JCPDS file NO. 29-0713) and a mixed phase of α-FeOOH and Fe_3O_4, respectively.

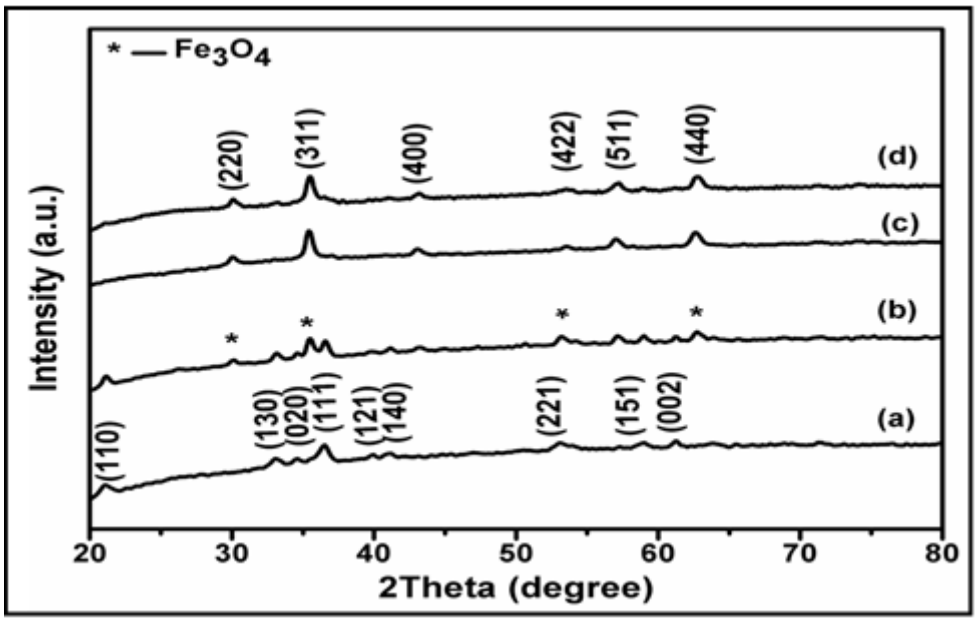

Fig.5.2 XRD results of the IONPs synthesized with $FeSO_4/FeCl_3$ at various pH values (a)6, (b) 8, (c) 10 and (d) 12.

Whereas the material prepared at pH of 10 and 12 exhibited a Fe_3O_4structure. The low intensity peaks with increasing pH of the medium was observed due to the decrease in the particle size (from FESEM observation) of the as-synthesized materials.

It is inferred that, at acidic reaction condition (pH 6) the goethite phase was achieved. When the basicity of the solution was slowly increased to pH 8, then the goethite and magnetite phases coexist [3]. Later, when the pH was around 10 pure form of magnetite observed due tothe homogeneous nucleation of ferrous and ferric ions. Further increase in pH value to 12, observed that the increase in intensity of the peaks showing increased crystallinity of the final product [4]. The average crystallite size was calculated using the Scherer formula [see in Eq. (2.2)] and is found to be in the range of 16-20 nm. The reaction condition and its corresponding crystallite sizes were shown in Table–5.1.

Table–5.1 The phase and crystallite sizes of IONPs prepared at different synthesis conditions.

Synthesis condition	Phase	Crystallitesize (nm)
100 °C	Magnetite	16
130 °C	Magnetite	15
160 °C	Magnetite	18
190 °C	Magnetite,Fe_2O_3	20
pH=6	Goethite	12
pH=8	Goethite, Magnetite	16
pH=10	Magnetite	15
pH=12	Magnetite	16

It can be seen that, when the reaction temperature is increased from 100-190 °C, there is slight increase in

crystallite size from 16-20 nm. Whereas, with increase in pH, the crystallitesize corresponded to magnetite phase did not show much variation. These results indicate thatthe reaction temperature greatly influences the crystallite size than the alkalinity of the reaction solution.

Morphological studies

The morphological studies of as-prepared INOPs carried out by FESEM were shown in Fig. 5.3 and Fig. 5.4. Fig. 5.3 (a-d) showed the morphology of synthesized materials at various reaction temperatures100,130,160 and190°C.The materials synthesized at 100, 130, and 160°C

Contain both spherical and rod shaped particles where as the material prepared at190°Ccontains only spherical particles(14–38nm).The FESEM images of the materials prepared at different pH (8, 10, and 12) conditions were shown in Fig. 5.4(a–c). All the materials exhibited spherical and rod shaped morphology. The diameter of the spherical particles ranged from 18 to 25 nm, whereas the diameter and length of the rod shaped particles were 11–20 nm and 80–188 nm, respectively. However, the particle size decreased with an increase in pH value. According to the earlier report, it is worth noting that there are no simple rules to determine the final shape of inorganic nanomaterials. The shape and size of the final product depends on the basic principle of nucleation and growth that typically occurs in the bulk solution throughout all the reactions. Nucleation and growth behavior can be varied by reaction conditions like concentration of the precursor or super saturation, reaction temperature and time etc.

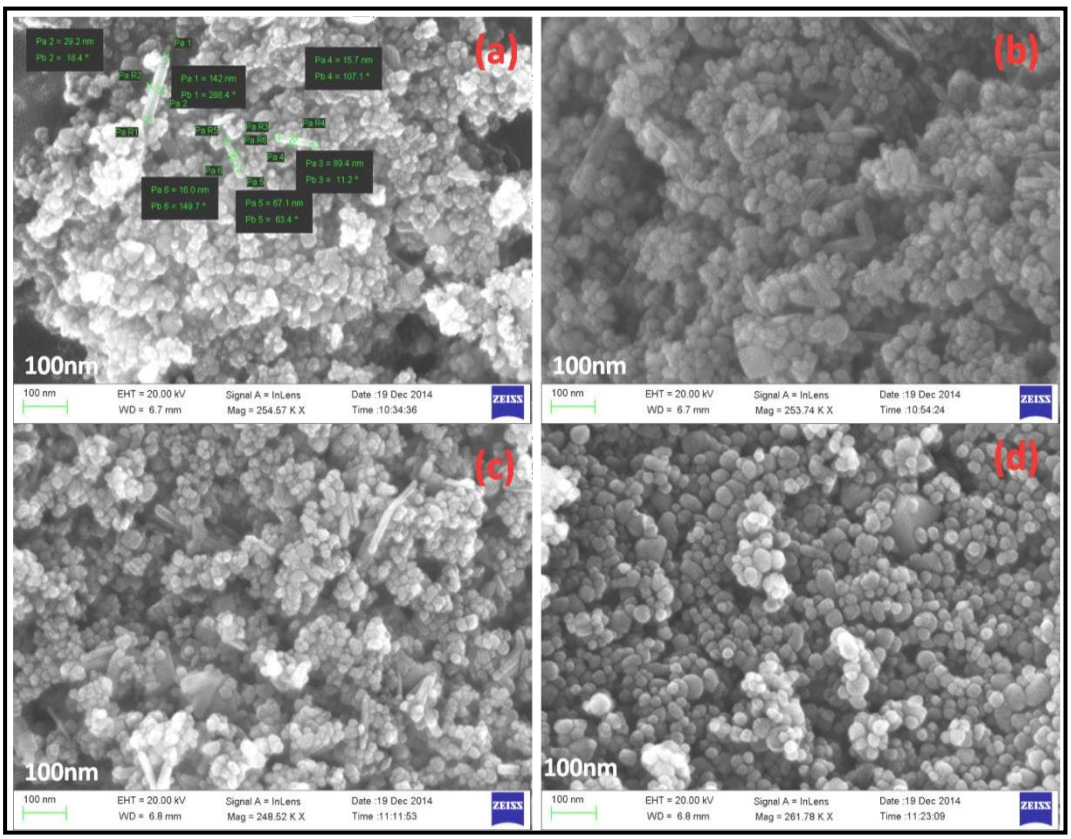

Fig.5.3 FESEM image of the IONPs prepared with $FeSO_4/FeCl_3$ at different hydrothermal temperatures (a) 100, (b) 130, (c) 160 and (d) 190 ºC.

Thus, to know the formation process and shape evolution strategy of inorganic nanomaterials, the influences of these reaction conditions during synthesis procedure is essential [5]. The Particle sizes

obtained from FESEM were tabulated in Table–5.2.

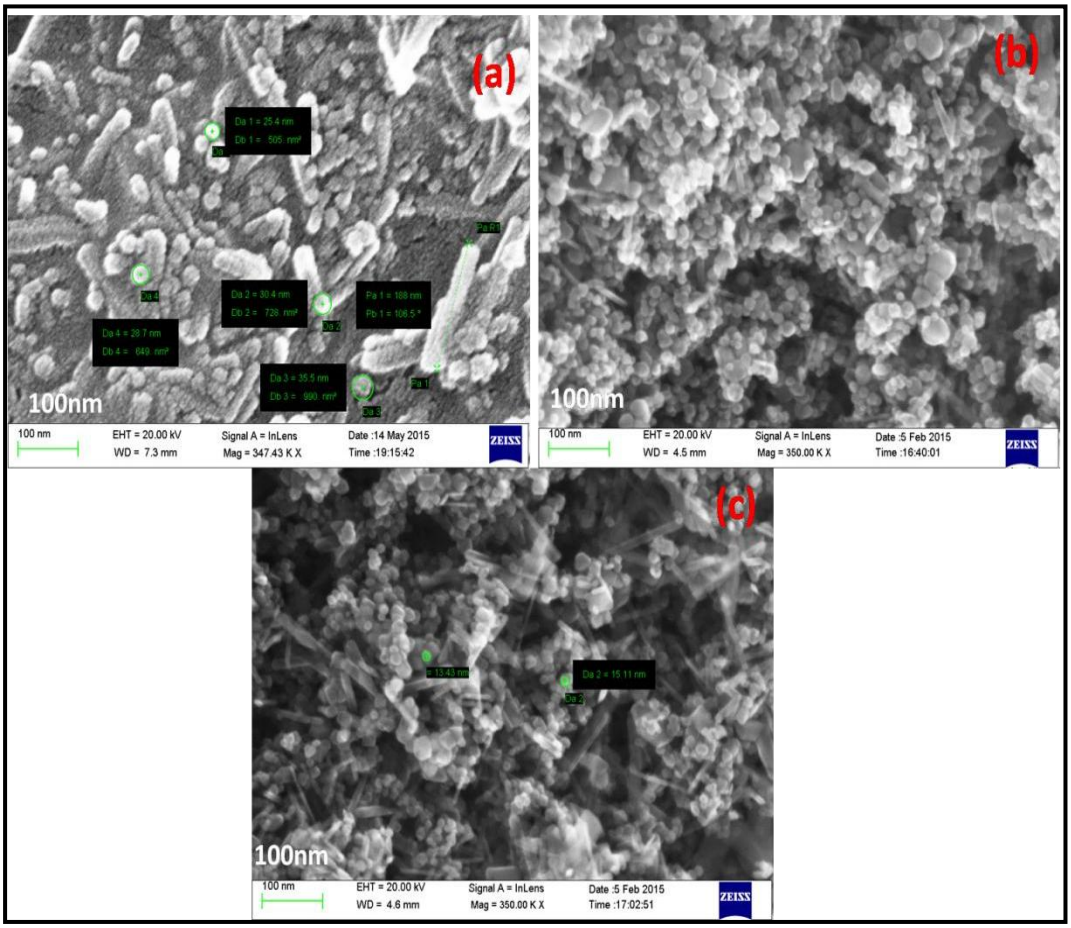

Fig.5.4 FESEM images of the powders prepared with $FeSO_4/FeCl_3$ at various pH conditions (a) 6, (b) 8, (c) 10 and (d) 12.

Table–5.2 The particle sizes of IONPs synthesized at different synthesis conditions.

Synthesis condition	Particlesize(nm)
100 ºC	S=14-37,R =140
130 ºC	S=20-36,R=150
160 ºC	S=20-39,R=190
190 ºC	S=18-25
pH=6	-
pH=8	S=25-35,R=188
pH=10	S=20-36,R=150
pH=12	S=13-15,R=100

here, S=Spherical and R=Rod length

Optical properties

The optical absorption properties of the hydrothermally synthesized IONPs at different hydrothermal temperatures, shown in Fig. 5.5 and the insets are Tauc plots of corresponding materials. The UV-vis. absorption spectra of the materials prepared at 100, 130 and 160 ^{o}C [Fig. 5.5(a-c)] showed maximum absorption edge around 380 nm, which is related to magnetite structure [6]. The absorption spectra of materials prepared at 190 ^{o}C [Fig. 5.5(d)] shows a red shift, which may be due to the presence of Fe_2O_3phase.

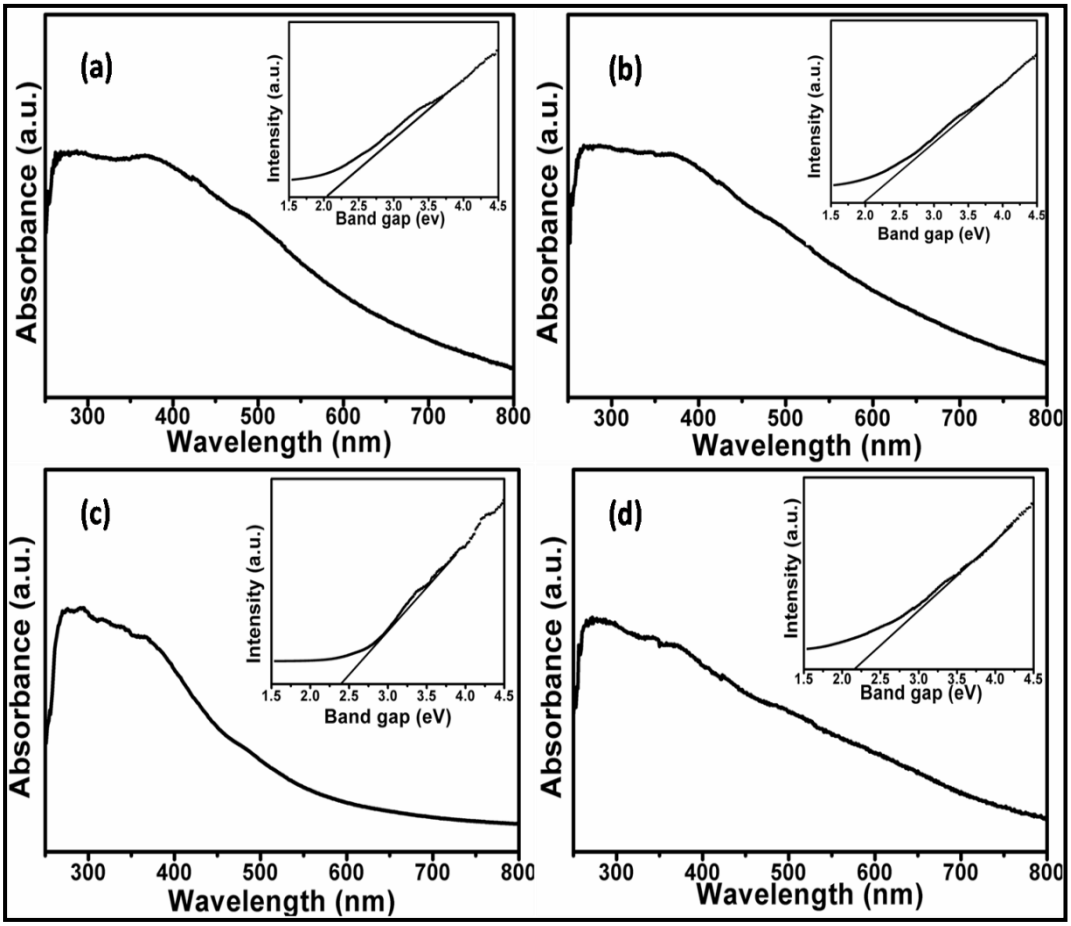

Fig. 5.5 UV-visible spectra of the IONPs prepared with $FeSO_4/FeCl_3$ salts at different hydrothermal temperatures(a)100, (b)130, (c)160 and (d)190ºC within sets representing Tauc plots.

UV-visible spectra of the IONPs prepared at various alkaline conditions were shown in Fig. 5.6. The materials prepared at pH 6 and 8 showed maximum absorption at 280 and 360 nm, respectively, indicating a α-FeOOH structure[7,8]. Cui*et.*al. reported a similar behavior and

attributed it to the absorption edge of a α-FeOOH [8]. The XRD results at pH 8 exhibits a mixed phase with higher percentage of goethite and lower percentage of magnetite phase. Concurrently the UV absorption result depicts that at pH 8 the goethite phase was dominant. The materials prepared at pH 10 and 12 [Fig. 5.6(a, b)] having similar absorption edge to that of the material prepared at hydrothermal temperature 130 ^{o}C, showing the magnetite structure. The optical band gap of as prepared IONPs were evaluated by Tauc plot equation (2.4).

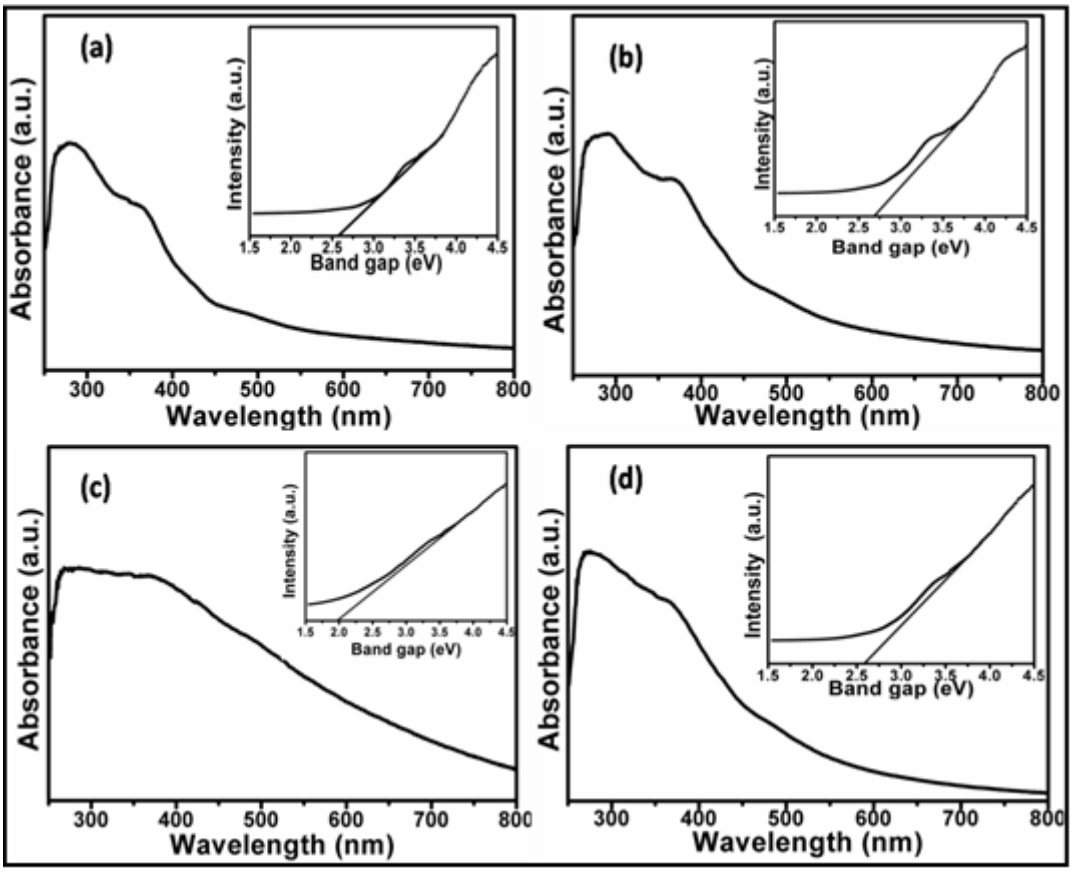

Fig.5.6 Optical properties of IONPs synthesized with $FeSO_4/FeCl_3$salt sat various pH conditions (a) 6, (b) 8, (c) 10 and (d) 12 with insets representing Tauc plots.

For evaluation of E_g value, a graph drawn between $(\alpha hv)^2$ vs. (hv) and the E_g values were estimated directly from the intersection of the straight line on the axis of photon energy(hv).The obtained E_g values are varying in the range of1.95–2.6 eV. These values are higher than the bulk iron oxides, since bulk magnetite of E_g=0.15 eV and bulk goethite of E_g= 2.1eV [9]. The higher band gaps may be attributed to the quantum confinement of the NPs of the prepared materials [10].

Magnetic properties

Fig. 5.7 shows the room temperature magnetic properties of IONPs prepared with $FeSO_4/FeCl_3$ salts at various hydrothermal temperatures (100, 130, 160, and 190 °C/18 hrs.) which were studied by VSM. The formation of hysteresis loop could not be observed, for the material prepared at different reaction temperatures, and at pH values, indicating SPM behavior. The room temperature magnetic properties of IONPs that synthesized with $FeSO_4/FeCl_3$ salts through hydrothermal method at different alkaline (pH 6, 8, 10 and 12) conditions were shown in Fig.5.8.

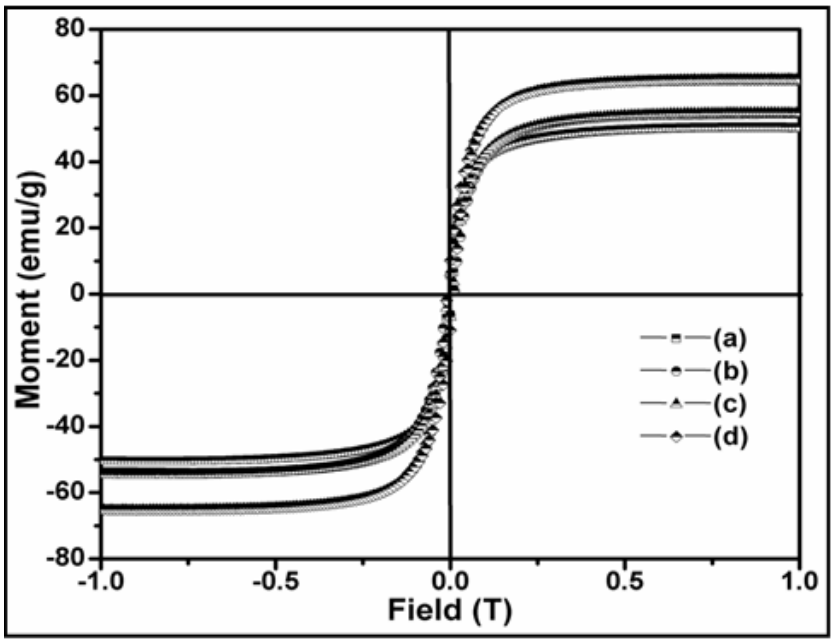

Fig.5.7 The room temperature magnetic properties of IONPs synthesized with $FeSO_4/FeCl_3$salts at various reaction temperatures (a) 100, (b) 130, (c) 160 and (d) 190 ºC.

The loop formation was not observed for the materials prepared at different reaction pH conditions. It indicates SPM behavior except inset hysteresis loop belongs to pH 6 with weak-ferromagnetic behavior due to the presence of goethite phase. The synthesized IONPs have lower H_C values, which is fairly in agreement with the earlier report [11]. The variations in M_S with reaction temperature and pH conditions were shown in Fig. 5.8(a and b). The increase in M_S with increased reaction temperature is due to improved particle size and phase transformation as observed from XRD analysis.

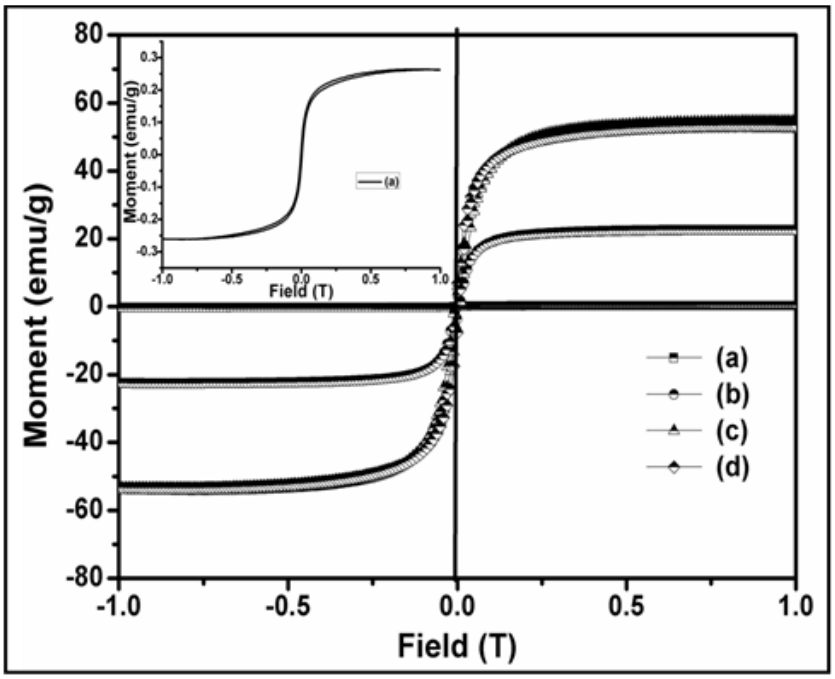

Fig.5.8 The room temperature magnetic properties of IONPs synthesized with $FeSO_4/FeCl_3$salts at various pH conditions (a) 6, (b) 8, (c) 10 and (d) 12.

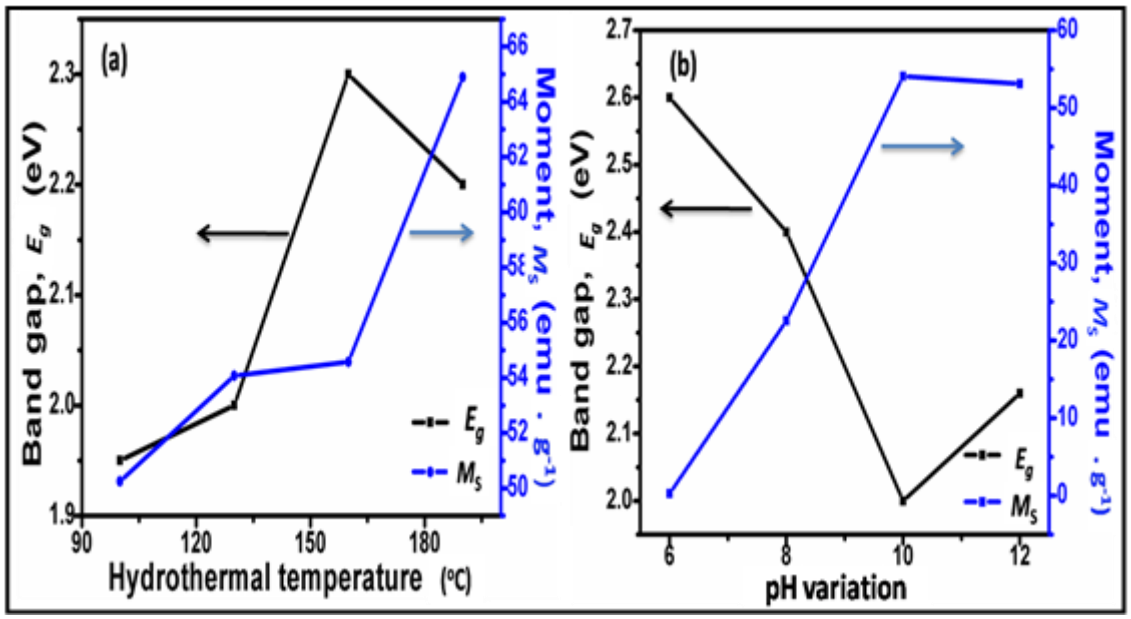

Fig.5.9 Variation between band gap values(a)and saturation magnetization values(b)at different temperatures and pH values.

Conclusions

Fe3O4 and a-FeOOH IONPs were successfully prepared using the hydrothermal method at different reaction temperatures and pH values. The samples prepared at 100, 130, and 160 8C exhibited magnetite structure, whereas the sample prepared at 190 8C exhibited a small extra XRD peak related to the a-Fe2O3 phase. The samples prepared at pH of 6 and 8 displayed an a-FeOOH and multi-phase structure respectively, but the samples prepared at pH of 10 and 12 displayed an Fe3O4 structure. FESEM analysis revealed that all samples contained sphere and rod shaped particles, except the sample prepared at 1908C only had spherical particles. The results demonstrate that the IONPs prepared at 130 8C/pH = 10 and 190 8C exhibited higher saturation magnetization, making these potential materials for biomedical and sensor applications.

Acknowledgement: Author is thankful to the Department of Nanoscience, UOH, for providing the facilities to do the research work, and Dept of Physics mvs (A) for conduction of project in the lab.

Conflict of Interest: Author has no conflict of interest.

References

[1] A.K. Nikumbh, R.A. Pawar, D.V. Nighot, G.S. Gugale, M.D. Sangale, M.B. Khanvilkar, A.V. Nagawade: J. Magn. Magn. Mater. 355 (2014) 201 – 209. DOI:10.1016/j.jmmm.2013.11.052
[2] H.J. Song, X.H. Jia, X.Q. Zhang: J. Mater. Chem. 22 (2012) 22699 – 22705. DOI:10.1039/C1JM13233D
[3] M.K. Sinha, S.K. Sahu, P. Meshrama, L.B. Prasad, B.D. Pandey: Powder Technol. 276 (2015) 214 – 221. DOI:10.1016/j.powtec.2015.02.006
[4] W. Wu, C. Jiang, V.A.L. Roy: Nanoscale 7 (2015) 38 – 58. DOI:10.1039/C4NR04244A

[5] W. Wu, Z. Wu, T. Yu, C. Jiang, W.S. Kim: Sci. Technol. Adv. Mater. 16 (2015) 023501. DOI:10.1088/1468-6996/16/2/023501
[6] H. Karami: J.Cluster Sci.21 (2010) 11 – 20. DOI:10.1007/s10876-009-0278-x
[7] P.L. Hariani, M. Faizal, Ridwan, Marsi, D. Setiabudidaya: Int. J. Environ. Sci. Dev. 4 (2013) 336 – 340. DOI:10.7763/IJESD.2013.V4.366
[8] E.H. Kim, H.S. Lee, B.K. Kwak, B.K. Kim: J. Mag. Magn. Mater. 289 (2005) 328 – 330. DOI:10.1016/j.jmmm.2004.11.093
[9] D.S. Mathew, R.S. Juang: Chem. Eng. J. 129 (2007) 51 – 65. DOI:10.1016/j.cej.2006.11.001
[10] Y.C. Han, H.G. Cha, C.W. Kim, Y.H. Kim, Y.S. Kang: J. Phys. Chem. C 111 (2007) 6275 – 6280. DOI:10.1021/jp067558z
[11] S. Ahmadi, C.H. Chia, S. Zakaria, K. Saeedfar, N. Asim: J. Mag. Magn. Mater. 324/2012) 4147 – 4150. DOI:10.1016/j.jmmm.2012.07.023
[12] M. Hojamberdiev, G. Zhu, A. Eminov, K. Okada: J. Cluster Sci. 24 (2013) 97 – 106. DOI:10.1007/s10876-012-0522-7
[13] D. Li, W.Y. Teoh, C. Selomulya, R.C. Woodward, P. Munroe, R. Amal: J. Mater. Chem. 17 (2007) 4876 – 4884. DOI:10.1039/B617280F
[14] H. Iida, K. Takayanagi, T. Nakanishi, T. Osaka: J. Colloid Interface Sci. 314 (2007) 274 – 280. DOI:10.1016/j.jcis.2007.05.047
[15] MD. Shariful Islam, Y. Kusumoto, J. Kurawaki, MD. Abdulla-AlMamun, H. Manaka: Bull. Mater. Sci. 35 (2012) 1047 – 1053. DOI:10.1007/s12034-012-0414-3
[16] Z. Wu, S. Yang, W. Wu: Nanoscale 8 (2016) 1237 – 1259. DOI:10.1039/C5NR07681A
[17] S.A. Kulkarni, P.S. Sawadh, P.K. Palei: J. Korean Chem. Soc. 58 (2014) 100 – 104. DOI:10.5012/jkcs.2014.58.1.100
[18] F.N. Sayed, V. Polshettiwar: Sci. Rep. 5 (2015) 09733. DOI:10.1038/srep09733
[19] X. Cui, T. Liu, Z. Zhang, L. Wang, S. Zuo, W. Zhu: Powder Technol. 266 (2014) 113 – 119. DIO: 10.1016/j.powtec.2014.06.028. DOI:10.1016/j.powtec.2014.06.028
[20] G. Rana, U.C. Johri: Adv. Mater. Lett. 5 (2014) 280 – 286. DOI:10.5185/amlett.2014.10563
[21] B.K. Pandey, A.K. Shahi, Jyoti Shah, R.K. Kotnala, R. Gopal: Appl. Surf. Sci. 289 (2014) 462 – 471. DOI:10.1016/j.apsusc.2013.11.009
[22] S. Ahmadi, C.H. Chia, S. Zakaria, K. Saeedfar, N. Asim: J. Magn. Magn. Mater. 324 (2012) 4147 – 4150. DOI:10.1016/j.jmmm.2012.07.023
[23] X.N. Xua, Y. Wolfus, A. Shaulov, Y. Yeshurun, I. Felner, I. Nowik, Yu. Koltypin, A. Gedanken: J. Appl. Phys. 91 (2002) 4611 – 4616. DOI:10.1063/1.1457544