

Zinc Ferrite Nanoparticle Synthesis and Characterization; Effects of Annealing Temperature on the Size of nanoparticles

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Abstract: Zinc ferrite nanoparticles have been synthesized by co-precipitation method from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Oleic acid was used as surfactant and the reaction was carried out in basic medium by using sodium hydroxide solution. The nanoparticles synthesized were annealed at different annealing temperatures of 500 °C, 600 °C, 800 °C, and 900°C. The size of nanoparticles was also analyzed at a constant annealing temperature for different duration of time. X-ray diffraction pattern confirmed the formation of single-phase nanoparticles of zinc ferrite. Fourier transform infrared study was performed to ascertain the structure of the nanoparticles. FT-IR studies also supported the trend of increasing size as shown by XRD results. The study revealed that size of the nanoparticles increased linearly with increasing annealing temperature due to coercivity, while there was no remarkable change in size by the duration of the annealing temperature.

Key words: nanoparticles, chemical synthesis, XRD, FT-IR

INTRODUCTION

Ferrite nanoparticles are under intense research because of their unique chemical, mechanical and structural properties (Dariel, M., *et al.*, 1987). Ferrite nanoparticles have versatile application in catalysis, electronics, photonics, sensors and ferro fluids (Guo, R., *et al.*, 2010; Hakuta, Y., *et al.*, 2005; Sivakumar, P., *et al.*, 2011). Ferrite nanoparticles are also used in biomedical sciences. Due to their unique size and shape, they can easily reach to the body parts where other conventional drugs find hard to reach. Size of the particles depends mostly on the preparation method and conditions. In The literature, there are a number of methods like as hydrothermal synthesis, mechanical Milling and hydrolysis of metal carboxylate in organic solvent can be used for the synthesis of nanoparticles (Hadjipanayis, G.C., R.W. Siegel (Eds.), 1994; Mojumdar, S.C., *et al.*, 2005). Every method has the merits and demerits regarding the control of particles size and durability.

Ammar *et al.*, (2006), prepared zinc ferrite nanoparticles by forced hydrolysis in a polyol medium. They reported that the magnetization was increased with decreasing the size of the zinc ferrite nanoparticles. Yang *et al* (2008), synthesized zinc ferrite nanoparticles by the tartrate precursor method. They reported that stoichiometry and phase purity of zinc ferrite nanoparticles are affected by intermediate phases during preparation of nanoparticles. Drogenik *et al.*, (2008) synthesized zinc ferrite nanoparticles by using ultrasonic radiation. They reported that zinc ferrite nanoparticles prepared by ultrasonic radiations have highest saturation magnetization because of the substitution of Fe^{+3} by Zn^{+2} upto molecular composition of $\text{Zn Fe}_2\text{O}_4$. Bardhan *et al.*, (2010), synthesized zinc ferrite nanoparticles by solid-state combustion method. They found that conductivity decreased with decreasing the particle size. Swamy *et al.*, (2011) prepared zinc ferrite nanoparticles by self-propagating low-temperature combustion method. They reported that the average size of the particles was 40 nm. They also reported that this is a low cost method which can be used to synthesize other metal ferrite and mixed metals ferrite nanoparticles.

In the present work zinc ferrite nanoparticles have been synthesized by wet chemical method. The product was annealed at different temperature, to study the variation in particle size. In addition the size variation was also studied as a function of duration of annealing conditions.

Experimental:

2.1 Materials:

Iron nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sodium hydroxide NaOH and oleic acid purchased from Merck, were of purity 98-99%. The chemicals were used without further purification.

2.2. Experimental Procedure:

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Zinc ferrite nanoparticles were synthesized by co-precipitation method, using starting material of iron nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Figure 1). Oleic acid was used as a surfactant to prevent the agglomeration of nanoparticles. 30 ml of 0.2 M zinc nitrate solution were mixed with 30 ml of 0.4 M iron nitrate solution in 500 ml beaker. The initial pH of the solution was noted as 1.14 because of the presence of nitric and nitrous acids. The solution was constantly stirred with the help of magnetic stirrer. 10-15 ml of 3 M solution of NaOH was added drop wise to adjust the pH of solution 11-12, with constant stirring. The reaction is carried out in higher values of pH, because in this pH range the size of the particles as well as their nucleation rate is controlled (Jolivet, J.P., *et al.*, 1997). A little amount of oleic acid 4-5 drops were added to the solution. Oleic acid prevents the agglomeration of the nanoparticles. The solution was then brought to reaction temperature of 80°C. The solution was stirred for 60 minutes and subsequently cooled to room temperature. The solution was decanted and washed twice with distilled water and finally with ethanol to remove the impurities and excess surfactant. The as-synthesized nanoparticles were centrifuged for 15 minutes at 3500 rpm and dried overnight at 105°C. The dried particles were milled in agate mortar. The powder nanoparticles were annealed at different temperatures of 500 °C, 600 °C, 800 °C, and 900°C for 4 hours and also for different time interval at the same annealing temperature of 800°C.

2.3. Characterization:

Structure and crystallinity of synthesized nanoparticles was analyzed by X-ray diffraction technique (XRD). The formation of zinc ferrite nanoparticles was confirmed by Fourier transform infrared (FT-IR) studies. X-ray diffraction (XRD) data was collected at room temperature on a Bruker D8 Advance Diffractometer using monochromatic Cu K_α radiation. Crystallographic properties e.g. phase of the material and crystal structure was determined using the same equipment.

FT-IR analysis was carried out by using Perkin-Elmer spectrum one instrument in the range of 4500-100 cm^{-1} . The samples were pelleted with KBr.

RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD) Analysis:

The X-ray diffraction patterns of zinc ferrite (ZnFe_2O_4) nanoparticles annealed at different temperatures are shown (Figures 2-6). The XRD spectra showed all the characteristics peaks corresponding to the characteristic planes (311), (511) and (440) appear at 35°, 57° and 64° (Girshick, L., P. Chiu, 1990), of Zinc ferrite nanoparticles with JCPDS card No. 82-1049. Fig. 2 shows a typical X-ray diffraction pattern of a ZnFe_2O_4 , well-defined diffraction peaks, confirming the formation of zinc ferrite nanoparticles. The sample was calcined at 500 °C, hence less crystallinity is observed in this spectrum. Figure 3 shows the XRD spectra of zinc ferrite nanoparticles calcined at 600 °C. The spectra shows that zinc ferrite nanoparticles are more crystalline at this temperature. The peak is sharper and narrower as compared to figure 2 spectra. The sharpness of the XRD spectra shows that crystallinity is increased with increasing the annealing temperature. The peak study of the spectra XRD spectra of zinc ferrite nanoparticles calcined at 800 °C (Figure 4), shows that peaks are sharper at this temperature as compared to the previous peaks. This trend can also be observed by analyzing the XRD spectra of zinc ferrite nanoparticles calcined at 900 °C (Figure 5). The sharpness of the XRD peaks is maximum for this spectra out of all the spectra recorded in this study. The sharpness of the peaks is also a good indicator for the increased size of the nanoparticles, as the particle size is increased by increasing the sharpness of the peak (Sui, Y.P., *et al.*, 2003). By increasing the annealing temperature, the diffraction peaks become sharper and narrower and increase in intensity. This is because of the amplification in crystallinity that leads to the increased particle size of the nuclei (Sui, Y.P., *et al.*, 2003). Hence, a maximum particle size of 51 nm was observed for zinc ferrite nanoparticles at this temperature. Figure 6 shows the XRD spectra of zinc ferrite nanoparticles calcined at different temperatures. It is evident from the XRD Pattern that crystallinity of ferrite nanoparticles is increased by increasing the annealing temperature.

3.2. Particle Size Calculation of Zinc ferrite nanoparticles by Scherrer formula:

The size of the zinc ferrite nanoparticles at different annealing temperatures was calculated using Scherrer equation for the [311] diffraction peak (Cornell, R.M., U. Schwertmann, 1996)]

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where D is the particle size, λ is the X-ray wavelength (1.5418), θ is the Bragg angle and β is the half maximum width.. The size of nanoparticles obtained at different annealing temperature was measured as 9nm, 12nm, 26nm, and 51 nm for 500 °C, 600 °C, 800 °C, and 900°C annealing temperature for 4 hours respectively. It was also noted from XRD size calculation that different size of nanoparticles were obtained even for a constant annealing temperature but their percentage was very low.

Size of nanoparticles calculated by Scherrer formula is given in table 1. It is evident from the tabulated data that particle size is increasing from 9 nm to 51 nm with increasing the annealing temperature from 500 °C to 900 °C.

Table 1: Size of Zinc ferrite nanoparticles annealed at different Temperatures.

Sample ID	Annealing Temperature (°C)	Size (nm)
ZF1	500	9
ZF2	600	12
ZF3	800	26
ZF4	900	51

Table 2: Size of Nickel ferrite nanoparticles for different duration of time at same annealing temperature of 800 °C

Sample ID	Annealing Temperature (°C)	Duration of Annealing Conditions (Hours)	Size (nm)
ZFa	800	6	26
ZFb	800	8	27
ZFc	800	10	25
ZFd	800	12	29

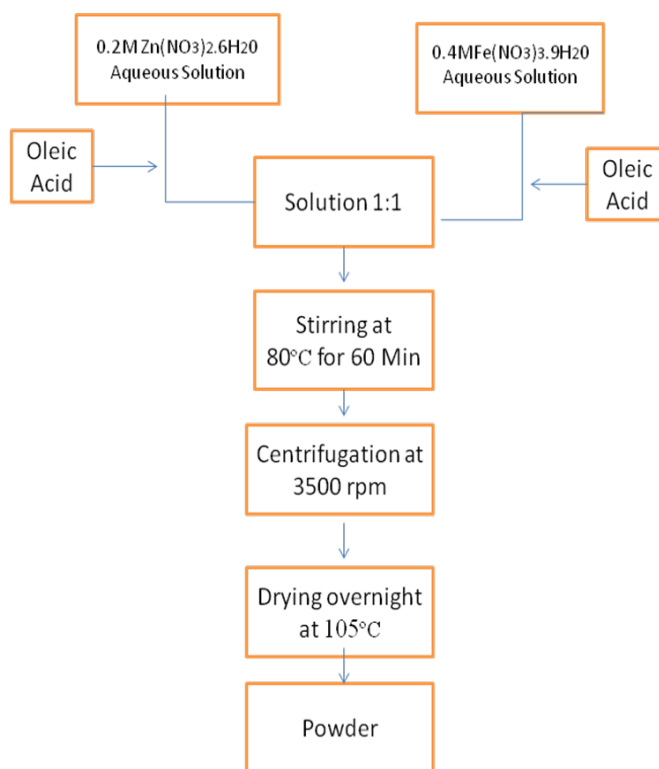


Fig. 1: Block diagram to obtain Zinc ferrite nanoparticles

3.3. Effect of Duration Of Annealing Temperature On The Particle Size Of Zinc Ferrite Nanoparticles:

Size of nickel ferrite nanoparticles as a function of duration of annealing temperature was also studied by XRD diffraction peak at the same annealing temperature of 800°C. The results in Table 2 showed that the particle size of 26nm, 27nm, 25nm and 29 nm for the annealing time duration of 6 hours, 8 hours, 10 hours and 12 hours, respectively. These results indicate that there is no remarkable change in size with the variation of duration of annealing condition.

3.4. Fourier transform infrared (FT-IR) Studies:

The formation of spinel $ZnFe_2O_4$ structure in the calcined zinc ferrite nanoparticles is further supported by FT-IR spectra shown (Figure 7-10). The peaks at 556 cm^{-1} correspond to the metal–oxygen (Fe–O) stretching vibrations and it is the characteristic peak of the spinel structure of zinc ferrite (Rao, G.S., *et al.*, 1970). The FT-IR band at 1378 cm^{-1} is due to stretching vibration of C-H bond of the oleic acid, which is used as a surfactants (Ibrahim1, M., *et al.*, 2006). This band disappeared when the samples were calcined at higher temperature. The

peak at 3450 corresponds to the vibration of O-H and the light band at 1640 could be attributed to the adsorbed water or humidity (Jalaly, M., *et al.*, 2009). This was further supported by disappearance of these bands at higher temperature. The strong absorption band at 426 cm^{-1} is ascribed as the stretching modes of Zn-O (Lepot, N., *et al.*, 2007; Kwon, Y.J., *et al.*, 2002).

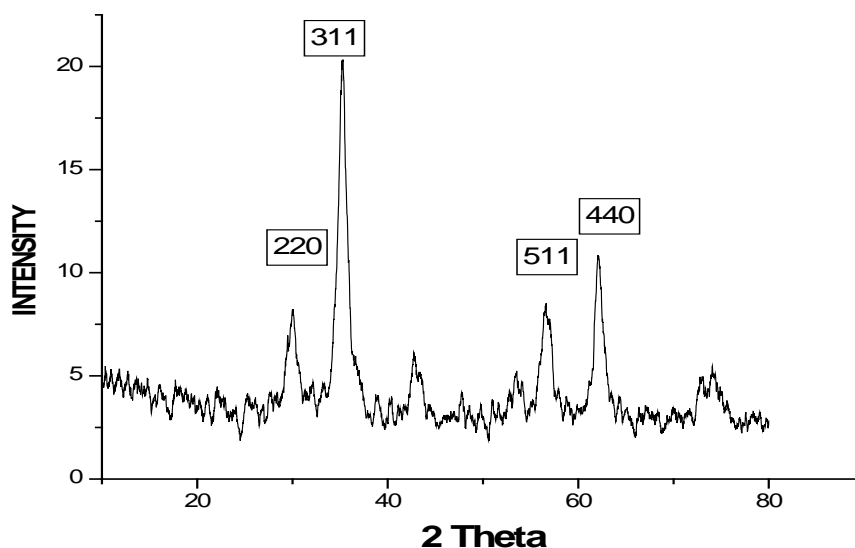


Fig. 2: XRD Spectra of Zinc ferrite nanoparticles calcined at 500 °C for 4 Hours.

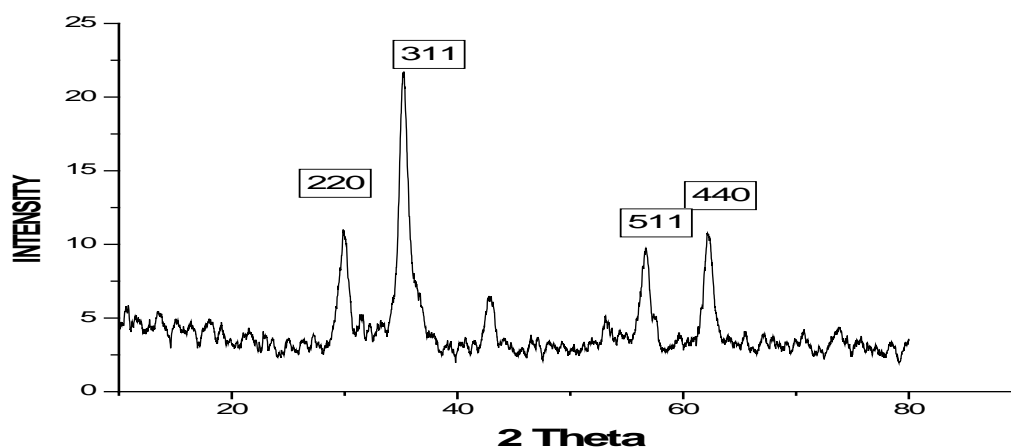


Fig. 3: XRD Spectra of Zinc ferrite nanoparticles calcined at 600 °C for 4 Hours.

3.5 Particle Size estimation of Zinc ferrite nanoparticles by FT-IR:

Although FT-IR cannot be used for the particles size calculation but the trend in the particles size can be analyzed by FT-IR spectra. Absorption band of a particular bond is shifted to the higher frequency when the size of the particles is increased (Mary kutty Thomas, S.K., K.C. Ghosh, 2002). In the current study, the absorption bands for $[\text{Fe} \leftrightarrow \text{O}]$ were observed at ~ 550 , ~ 556 , ~ 561 , and $\sim 570\text{ cm}^{-1}$ for the zinc ferrite nanoparticles calcined at 773, 873, 1073 and 1173 K respectively. Similarly, absorption bands for $[\text{Zn} \leftrightarrow \text{O}]$ were noted at ~ 424 , ~ 432 , ~ 436 and $\sim 445\text{ cm}^{-1}$ for the zinc ferrite nanoparticles calcined at 773, 873, 1073 and 1173 K respectively (Figure 7-10). This shifting of absorption bands clearly suggest the increase in the size of the particles as the annealing temperature is increased. These results strongly support the results of XRD data.

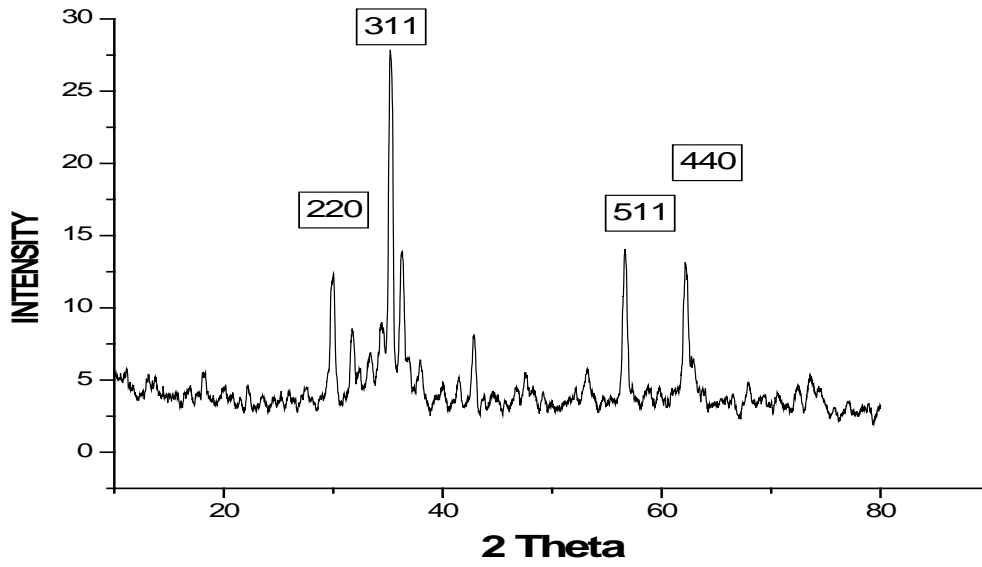


Fig. 4: XRD Spectra of Zinc ferrite nanoparticles calcined at 800 °C for 4 Hours

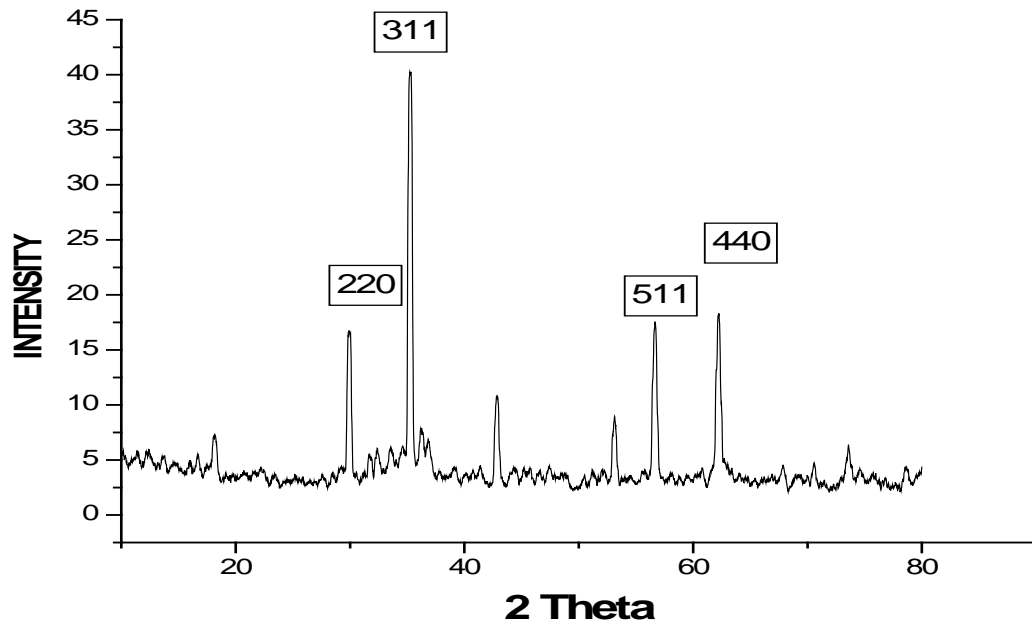


Fig. 5: XRD Spectra of Zinc ferrite nanoparticles calcined at 900 °C for 4 Hours

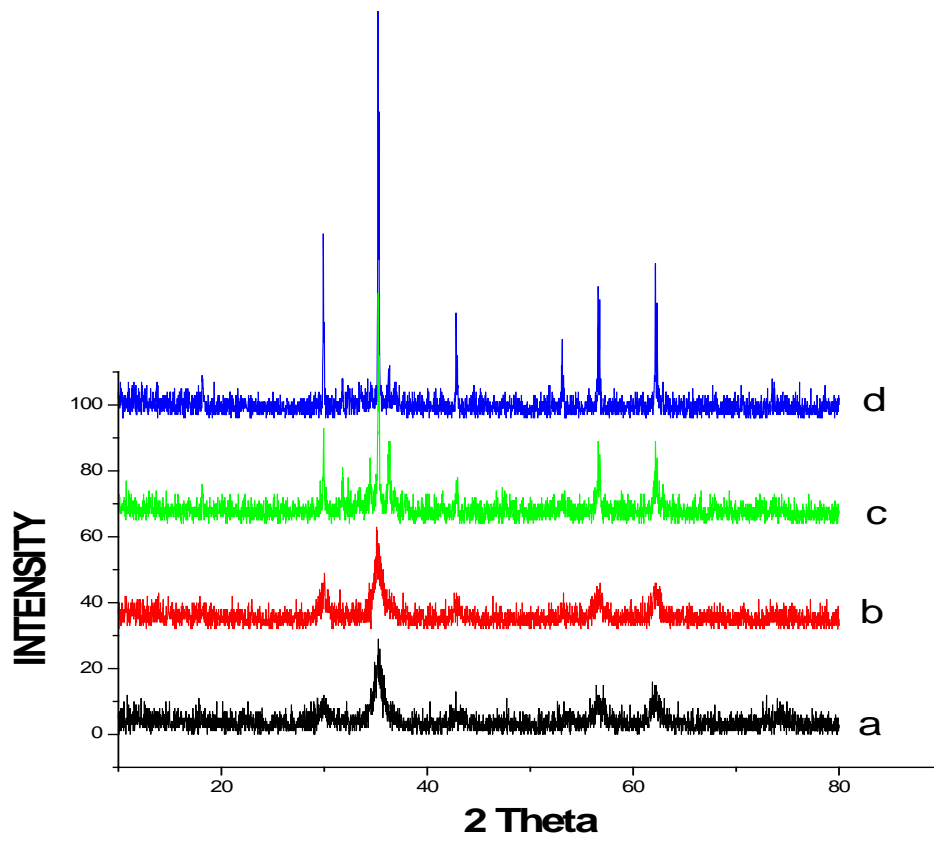


Fig. 6: XRD Spectra of Zinc ferrite nanoparticles calcined at (a) 500 °C, (b) 600 °C, (c) 800 °C and (d) 900 °C for 4 Hours.

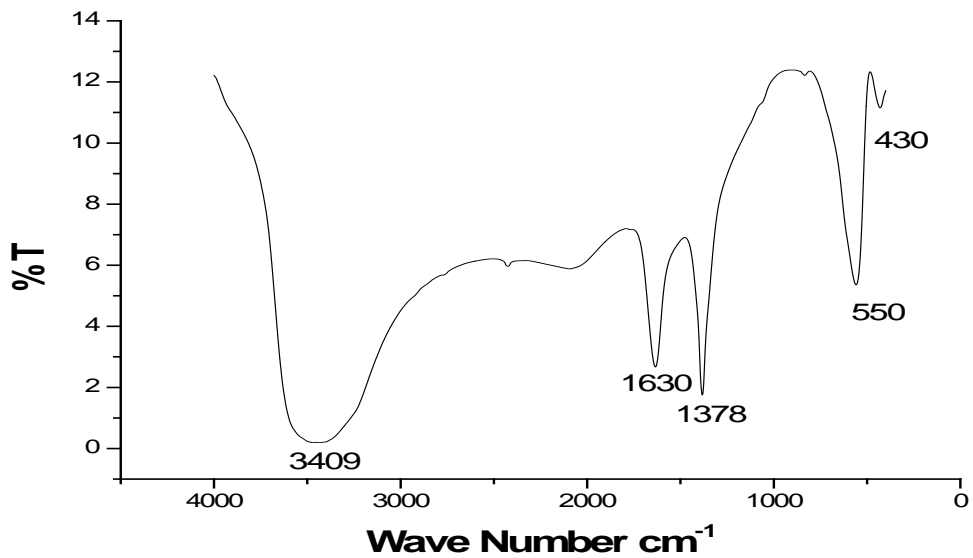


Fig. 7: FT-IR Spectra of Zinc ferrite nanoparticles calcined at 500 °C for 4 Hours

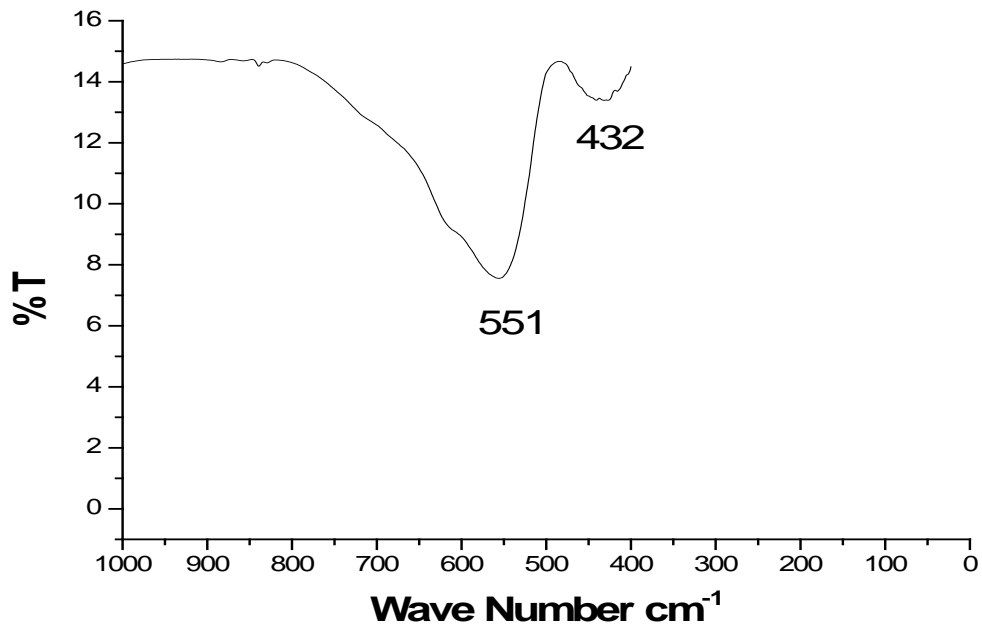


Fig. 8: FT-IR Spectra of Zinc ferrite nanoparticles calcined at 600 °C for 4 Hours

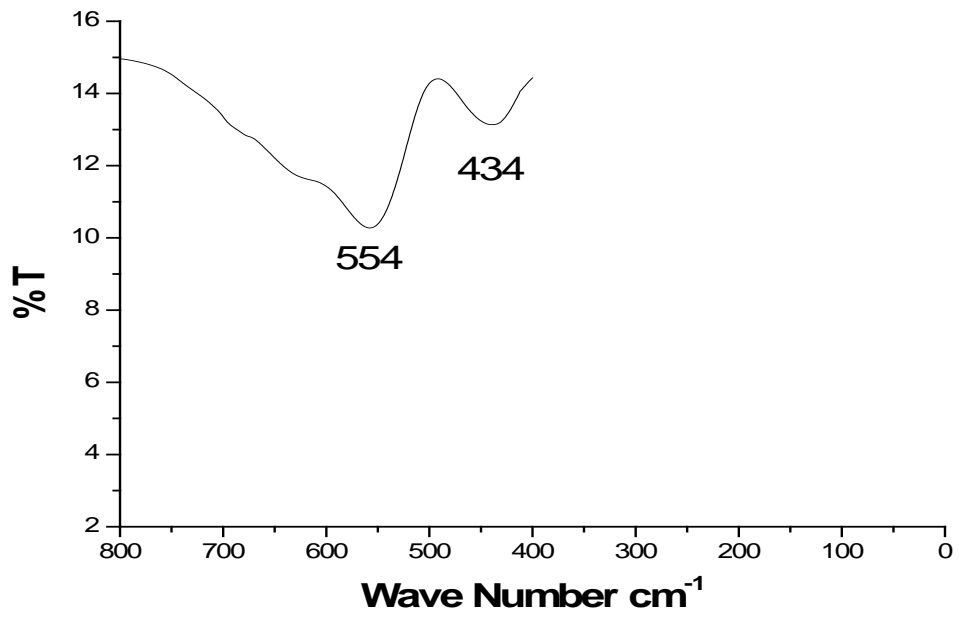


Fig. 9: FT-IR Spectra of Zinc ferrite nanoparticles calcined at 800 °C for 4 Hours

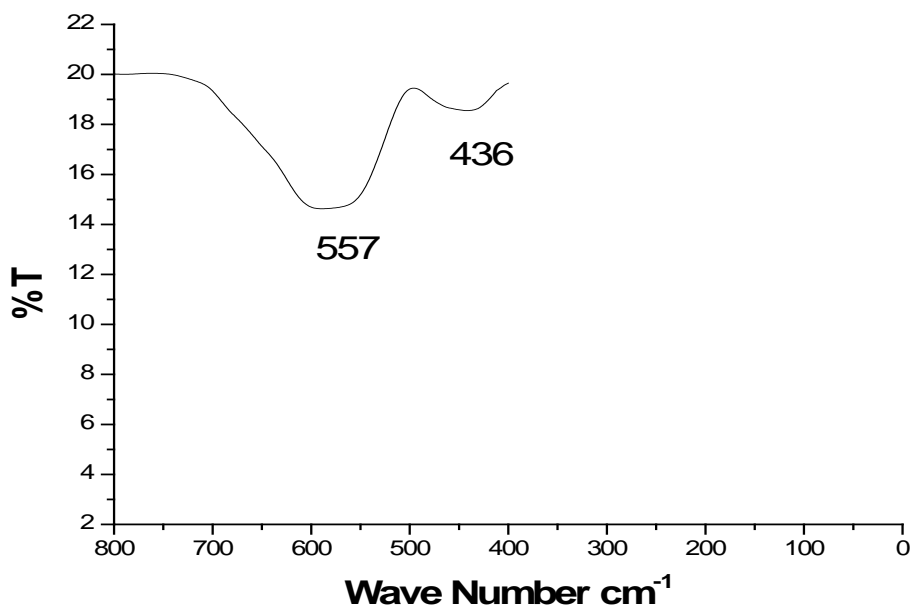


Fig. 10: FT-IR Spectra of Zinc ferrite nanoparticles calcined at 900 °C for 4 Hours

Conclusion:

Nanosized zinc ferrite particles were synthesized by co-precipitation methods at different annealing temperatures to analyze the effect of annealing temperature on the particle size of the compound. The structure of the compounds was confirmed by XRD. FT-IR analysis supported the formation of spinel structure of ferrite nanoparticles. The FT-IR spectra showed two characteristic metal oxygen vibrational bands, a Fe-O band, and Zn-O band.

Sherrer formula was utilized for the estimation of size of the zinc ferrite nanoparticles. Particles size of 9 nm, 12 nm, 26 nm and 51 nm were found at annealing temperature of 500 °C, 600 °C, 800 °C and 900 °C respectively. The study shows that the particle size increases with increasing annealing temperature. The study of size of zinc ferrite nanoparticles calcined at the same temperature for different duration of time, revealed that there is no remarkable change in the size takes place.

ACKNOWLEDGEMENT

Financial assistance from Kohat University of Science and Technology is gratefully acknowledged.

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