Effect of UV radiations to control particle size of Mn–Zn spinel ferrite nano-particles

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Abstract. Mn\textsubscript{x}Zn\textsubscript{1−x}Fe\textsubscript{2}O\textsubscript{4} (0.0 \leq x \leq 1.0) ferrite nano particles were synthesized for concentration varying from 0.27 to 0.87 to obtain chemically homogenous powder for obtaining fine particle size by co precipitation technique. Keeping in view the interest of scientists for particle size, the present work focus on the impact of UV radiation to control the particle size of prepared fine magnetic particles. The particles were digested for ninety minutes at a temperature of 90\degree C. The samples were divided into four equal quantities and were subjected to different doses of UV radiation.  The chemically produced samples of Mn–Zn ferrite nano particles were analyzed by XRD which confirmed cubic spinel structure of the material. The average crystallite size (t), lattice parameter (a) and other structural parameters of UV-irradiated Mn\textsubscript{x}Zn\textsubscript{1−x}Fe\textsubscript{2}O\textsubscript{4} spinel ferrite were calculated from XRD data. The spinel peak of the irradiated sample when compared with the control sample, shifted from 35.38 to 35.15. In few samples, additional peaks supporting the ferrite structure were also observed. The variation in the particle sizes observed for various doses of UV irradiation were in the range of 17.6 to 6.2 nm, whereas the particle size of the control was 8.82nm. The experiment was repeated for different concentrations, at the same digestion temperature and time revealed the similar results indicating that UV radiations can have a remarkable effect to control the phase and size of nano size fine magnetic ferrite particles. The present work successfully document the impact of UV to control the particle size.

1. Introduction
The “nano” prefix to technical terms is not simple replacement of the unit of Angstroms; this is a change in Science & Engineering. The world is attain in gun believable achievements because we are capable to figure things that work better on the minimum possibly attained length scales, atom by atom. Nano scaled items in its advanced form has major impact on almost industrial scale and all disciplines of society. It will offer better built, longer lasting, cleaner, safer, and smarter products for home, communications, medicine, transportation, agriculture, and for industry in general [1].

The production of ferrites nanoparticles has driven the research field on contemporary track and these nano-things will revolutionize industries and our lives. Soft ferrite cores are oxides made from Iron (Fe), Manganese (Mn), and Zinc (Zn) which are commonly referred to as manganese zinc ferrites.
They have a low coercivity and are also known as soft magnetic ferrites [2]. Because of their comparatively low losses at high frequencies, they are extensively used in switched-mode power supply (SMPS) and radio frequency (RF) transformers and inductors, shielding and linear inductive components [3-5]. Ferrite cores for the high frequency power supply and high quality communication markets are produced in a variety of shapes and sizes for inductors, pulse transformers, high frequency transformers, and noise filters [6]. Notable characteristics of Magnetics ferrite materials are commercially important due to high magnetic permeability and good temperature properties [7].

The magnetic behavior, electrical behavior and structural properties changes with different synthesizing techniques with changing concentrations of cations. The prepared ferrites having same composition of ferrite particles but different preparation techniques show different electromagnetic behavior. Many methods are followed for production of less time consuming and high quality nanoparticles. The processes affect the microstructure, particle size, surface to volume ratio and permeability [1].

For the preparation of ferrites with high values of electromagnetism, many processing techniques are in practice including co-precipitation, sol-gel techniques, spray drying, hydrothermal methods and alcohol dehydration processes [8-13]. The co-precipitation technique has got great attraction for scientists for obtaining good microstructure, better electromagnetic properties and better results at lower temperatures, and not much time consuming property during sample preparation[6].

In the present research work, Manganese Zinc Ferrite nanoparticles (Mn_{x}Zn_{1-x}Fe_{2}O_{3}) were synthesized by co-precipitation technique to produce chemically homogeneous powder for obtaining fine particles. The concentration (x) were varied from 0.27 to 0.87 in four samples. The samples were prepared at same digestion temperature and then each sample was further divided into four equal quantities. The samples were subjected to electromagnetic (UV) radiations. X-ray diffraction (XRD) was used to determine particle size due to changing concentration of Mn & Zn. The particle size was measured using Scherer’s formula. It was observed that X-ray densities were decreased linearly by increasing concentration of Mn. The particle size of the particles was found to be affected by Manganese concentration, but not too extent. The minimum particle size was obtained at x=0.27 when irradiated for 6 hours. In order to get more uniform crystalline structure the calcination of a sample was done after the preparation of samples by co-precipitation method. For lowering the total anisotropy and getting the homogenize material calcination process was used. After calcination the effect of UV irradiation was also observed for getting small particle size [7].

1. Experimental details

Manganese Zinc ferrites (Mn_{x}Zn_{1-x}Fe_{2}O_{3}) magnetic particles were prepared by using co-precipitation method for getting homogeneous powder of fine particle size. The concentrations of x are 0.27, 0.47, 0.67 and 0.87. The least expensive and readily available salts used for the preparation of Mn-Zn ferrite are MnCl_{2}.4H_{2}O(Manganese Chloride tetra hydrated), ZnCl_{2} (Zinc Chloride) and FeCl_{3}. 6H_{2}O (Ferric Chloride hexahydrated). The [M’OH] was 0.5 for each sample; the concentrations of FeCl_{3} and NaOH were constant for all the samples. For each sample the ratio of Mn^{2+} and Zn^{2+} ions was taken 1:2. The molecular weights of different chemicals used were 197.9, 136.3, 270.5 and 40 respectively.

For two molar solution of Fe salt, 1 molar solution of combined Mn and Zn salts was used. The next step was the addition of base solution to salt until the pH 12 was attained. 1 mole of MnCl_{2}.4H_{2}O contains 1 mole of Mn, 1 mole ZnCl_{2} contains 1 mole of Zn, 1 mole of NaOH contains 1 mole of Na and 1 mole of FeCl_{3} 6H_{2}O contains 1 mole of Fe. All solutions were made in distilled and de-ionized water. All the salts MnCl_{2}.4H_{2}O, ZnCl_{2} and FeCl_{3}, 6H_{2}O with different quantities for different samples were dissolved in distilled water [16]. The volume of this solution was 150 ml. In another beaker 100 ml solution of NaOH was prepared. The morality was taken 1 mol. The beaker containing 150 ml salts of MnCl_{2}.4H_{2}O, ZnCl_{2} and FeCl_{3}, 6H_{2}O was placed on magnetic stirrer of vigorous stirring speed (60 rpm) at room temperature. The aqueous solution of beaker containing base was added drop by drop into beaker containing salt solution. The addition of base solution was continued until the pH 12 was obtained. This process of adding consumed about 60 minutes for each samples. After this addition the
final solution was about 250 ml. During the addition dark brown precipitates were obtained. The beaker containing the dark brown precipitates was positioned in a pre-heated water bath containing water. The temperature of water bath was kept constant at 90°C for each sample. Digestion was performed for 90 minutes for each sample. The prepared particles were settled down at the bottom of beaker. The beaker was cooled to the moderate temperature after taking out from water bath. The chemically prepared particles were attained via filtration. The filtered particles were dried at room temperature for 18 hours. Finally, the fine materials were produced and accumulated on the filter paper. Then purified samples were provided heat treatment in an oven at same temperature i.e. 100°C for 24 hours [17-18]. Each sample was then divided into four equal parts. One sample was taken as standard while the others are irradiated for 2 hrs, 4 hrs & 6 hrs respectively by UV source. The Similar process was adopted to prepare all the four samples. The spontaneous magnetization of particles was checked for all the samples with the help of permanent magnet. The prepared samples of manganese zinc ferrites were analyzes with the help of x-ray diffraction technique. The quantities of FeCl₃.6H₂O, ZnCl₂, MnCl₂.4H₂O and NaOH along with the metal to hydroxide ion concentration ratio are listed in table below:

| Sample No. | FeCl₃.6H₂O (per 50ml) | MnCl₂.4H₂O (per 50ml) | ZnCl₂ (per 50ml) | NaOH (per 100ml) | Digestion Time (Min) |
|------------|----------------------|-----------------------|------------------|------------------|---------------------|
| S1         | 2.70g                | 0.723g                | 0.183g           | 8g               | 90                  |
| S2         | 2.70g                | 0.525g                | 0.320g           | 8g               | 90                  |
| S3         | 2.70g                | 0.327g                | 0.457g           | 8g               | 90                  |
| S4         | 2.70g                | 0.117g                | 0.529g           | 8g               | 90                  |

Ultra-fine particles of MnₓZn₁₋ₓFe₂O₃ prepared by co-precipitation were analyzed by using X-ray diffraction [16]. Powder method was employed for this purpose. In this method, the specimen for diffraction is obtained by sticking some of the powdered materials onto the glass slide with trace of petroleum jelly. A narrow beam of parallel monochromatic X-ray impinges on specimen. The source of X-rays is Coolidge-type X-ray tube with a copper target, equipped with filter to remove all spectral components except desires Ka line. The diffracted radiation is detected by a photo-multiplier tube, which measures the diffracted beam intensities. The diffracted intensity is obtained when Bragg’s law is satisfied i.e. 2dSinθ=nl where ‘d’ is inter planer spacing. ‘θ’ is angle between the incident X-ray beam and diffracting beam plane. ‘L’ is wavelength of X-rays used.

By using d-values from the peak analysis of samples, the lattice constant were calculated using the relation a = d (h²+k²+l²)¹/² for cubic structure [19]. X-ray density was measured by using formula D₅ = 8 M/Na³. Since each primitive unit cell of the spinel structure contains 8 molecules, the value of the X-ray density, D₅ was determined in terms molecular weight(M), Avogadro no.(N)= 6.0225×10²³ atom/mole and lattice constant(a) [20]. Particle sizes of spinel peaks of all samples were calculated using Scherer’s equation [19, 21]. The main characteristic peak (311) for ferrites was used to estimate the particle size. The mean crystalline sizes were calculated from XRD line width of (311) peak using the Scherer equation (t = 0.9λ/B cosθ), where t is mean crystalline size, λ is X-ray wavelength B is he angular line width of half maxima intensity and θ is Bragg’s angle in degrees [21].

2. Results
Spinel structure ferrite belongs to technologically important materials. Fine Manganese Zinc Ferrite powders were prepared and then exposed to UV irradiation. The XRD analysis was made in order to determine the structure characterization, particle size, lattice constant and density.
Table 2. Showing the effect of UV irradiation on Particle Size, Lattice Constant, Density(X)

| UV Treatment Time (hrs) | Sample Code | Mn (X) Contents | Particle Size (nm) | Lattice Constant (Å) | Density (gm/cm³) |
|------------------------|-------------|-----------------|-------------------|----------------------|------------------|
| Un-Treated             | S1-A        | 0.27            | 8.82              | 8.43                 | 5.28             |
|                        | S2-A        | 0.47            | 17.64             | 8.47                 | 5.17             |
|                        | S3-A        | 0.67            | 6.57              | 8.43                 | 5.19             |
|                        | S4-A        | 0.87            | 8.82              | 8.40                 | 5.19             |
| 2 hr treatment         | S1-B        | 0.27            | 17.64             | 8.41                 | 5.32             |
|                        | S2-B        | 0.47            | 8.86              | 8.44                 | 5.22             |
|                        | S3-B        | 0.67            | 10.59             | 8.43                 | 5.20             |
|                        | S4-B        | 0.87            | 13.32             | 8.48                 | 5.05             |
| 4 hr treatment         | S1-C        | 0.27            | 7.23              | 8.40                 | 5.34             |
|                        | S2-C        | 0.47            | 13.22             | 8.45                 | 5.21             |
|                        | S3-C        | 0.67            | 8.83              | 8.42                 | 5.26             |
|                        | S4-C        | 0.87            | 7.24              | 8.42                 | 5.16             |
| 6 hr treatment         | S1-D        | 0.27            | 6.19              | 8.43                 | 5.28             |
|                        | S2-D        | 0.47            | 10.59             | 8.42                 | 5.26             |
|                        | S3-D        | 0.67            | 8.82              | 8.40                 | 5.19             |
|                        | S4-D        | 0.87            | 10.58             | 8.47                 | 5.07             |

3. Result discussions

4.1 X-Ray diffraction studies

From values given in Table 2 it could be observed that by increasing the time of ultra violet radiation, 2θ angle for characteristic spinel peak shifts showing precise spinel structure. It is concluded that ultra violet radiation have a remarkable effect on manganese zinc ferrites when the concentration of content is 0.27 & 0.67, while ultra violet radiation have no remarkable effect on manganese zinc ferrites when the concentration of content is 0.47& 0.87, but it was experienced that increase exposure to ultra violet radiation effect remarkably effect the structural properties of ferrites. The X-ray diffraction patterns for sample S3-A, S3-B, S3-C & S3-D are given as Figure 1 (a-d),

4.2 Lattice parameters

The results shown from Figure 2 indicate that the lattice parameter increases with increasing Mn ion contents. The increase of the lattice parameter can be attributed to the ionic radii of the ions. The value of the lattice constant for ZnFe₂O₄ was found to be 8.42 Å which is in good agreement with that obtained by JCPDS card where a = 8.44Å, while the value of lattice constant for MnFe₂O₄ was found to be 8.48Å. The measured lattice parameter for all samples changed from 8.40 to 8.48Å.
Figure 1 (a). XRD pattern of Mn-Zn ferrite without UV treatment

Figure 1 (b). XRD pattern of Mn-Zn ferrite after 2 hrs UV treatment

Figure 1 (c). XRD pattern of Mn-Zn ferrite after 2 hrs UV treatment

Figure 1 (d). XRD pattern of Mn-Zn ferrite after 2 hrs UV treatment

Figure 2. Graph between lattice constant and content (x)
4.3 X-Ray density
From the above data, it is clear that $D_x$ decreases with increasing $x$. The value of $D_x$ for $\text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ was found to be 5.34 to 5.07 gm/cm$^3$. The decrease of $D_x$ with Mn ion and Zn ion content could be attributed to the atomic weight and the radii of constituent ions, Figure 3.

![Graph between X-ray density and content (x)](image)

**Figure 3.** Graph between X-ray density and content (x)

4.3 Particle size
The X-ray densities decrease linearly by Mn concentration. The particle sizes of the samples were also affected by Manganese concentration. The minimum particle size (6.198) was obtained at $X = 0.27$ when it irradiated for 6 hours. The results showed that the lattice parameter increases with increasing Mn ion content Figure 4.

![Graph between Mn concentration and particle size (nm)](image)

**Figure 4.** Graph between particle size (nm) and content (x)

The increase of the lattice parameter can be attributed to the ionic radii of the ions. The results showed that co-precipitation technique was successfully used for the preparation of Manganese Zinc ferrites ($\text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$) magnetic particles where the concentrations $(X)$ are varying from 0.27 to 0.87. The samples were irradiated by ultra violet source and particle size was measured by Scherer’s formula. The XRD patterns of samples were found to be in agreement with the original patterns. In most samples Ultra violet showed the remarkable effect in improving the properties of Mn-Zn ferrites.

**Effect of calcination and UV irradiation**
The samples S3-A was calcined at 900°C and then divided into two equal parts. One part treated as standard and other was irradiated for 2 hours. The XRD pattern of pre irradiated and post irradiated
samples after calcination are shown in Figure 5 (a) and 5(b) respectively indicating the reduction in particle size from approximately 90 nm to 50 nm.

Figure 5(a). XRD pattern of calcined and untreated (UV) samples

Figure 5(b). XRD pattern of calcined and post Irradiated sample for 2 hrs

4. Conclusions
The consumption of ferrites is rapidly increasing with new advancement in electronics industry specifically power conversion and communication. The purpose of current study was to investigate the effect of UV radiations on the fabrication of Manganese Zinc Ferrite prepared using co-precipitation technique and achievement of lowest particle size along with better magnetic properties. Following are the findings:

1. The improvement in the existing techniques for fabrication of ferrites could be made by using UV treatment of samples and will also be helpful for exploration of new areas of research.
2. The single phase crystallite structure could be achieved with reduced particle size by increasing the time for UV treatment. By calcination and UV treatment, the counts of main peaks have been increased which shows improved crystalinity.
3. The unwanted peaks in XRD pattern analysis corresponds to impurities and secondary phases. With the help of UV treatment these could be reduced which alternatively means increase in phase formation.
4. The increase in Mn(x) concentration makes it possible to achieve high density Manganese Zinc ferrites.
5. The height of spinel peak of concentration achieved after calcination and then UV treatment compared to non-calcined and untreated sample shows the better magnetic qualities and better crystal structure.

6. References
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