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GREEN SYNTHESIS OF Cu-DOPED ZINC NANO FERRITE MATERIALS USING *Moringa Oleifera* LEAVES

Komal Yadav*, Gulzar Ahmed**, H.S. Chauhan***

ABSTRACT

Nanotechnology is an interdisciplinary area of research developing new nanoscale structures and examining their properties by altering the particle size, morphology and distribution. Nano-*ferrites have numerous applications in the field of biomedical, sensors, electronics, data and memory storage and many more due to its unique and novel properties. Present work focuses on the rapid, eco-friendly, inexpensive green synthesis over regular chemical routes for the preparation of most applicable ferrite nanoparticles. In this paper we show how we have prepared the Copper doped zinc ferrites nanoparticles* $Cu_xZn_{1-x}Fe_2O_4$ *(where x= 0.6 and 0.7) by green route method. Moringa oleifera extract (MOE) was used as a reducing and stabilizing agent for green route synthesis of ferrite nanoparticles. Their structural properties are characterized using X-ray diffraction (XRD). Dislocation density and strain were calculated by XRD analysis. The samples prepared shows crystalline nature and measure in nano range. The particle size of* $Cu_{0.6}Zn_{0.4}Fe_2O_4$ *sample was 9.11nm-20.96nm and for* $Cu_{0.7}Zn_{0.3}Fe_2O_4$ *sample particle size was 10.92nm-15.41nm.*

Keywords: Green route synthesis; ferrites, Moringa oleifera, nanoparticles, XRD.

INTRODUCTION

Magnetic nanoparticles are of vast technological importance due to their promising application as biosensors, biomedical, magnetic fluids, microwave absorbers, rechargeable lithium-ion batteries, and high-density data storage [1]. Spinel nanomaterials ferrites (SNF) are regarded as one of the most important inorganic nanomaterials because of their improved fundamental and unique properties [2, 3]. The physical and chemical properties of spinel

***Komal Yadav** is Assistant Professor, Department of Physics, Mewar University, Gangrar Chittorgarh, Rajasthan-312901. Corresponding email: komalyadav04041991@gmail.com

****Gulzar Ahmed** is Associate Professor, Department of Physics, Mewar University, Gangrar Chittorgarh, Rajasthan-312901

*****H.S.Chauhan** is Professor, Department of Physics,Mewar University, Gangrar Chittorgarh, Rajasthan-312901.

ferrites are different from their corresponding bulk materials due to their higher surface-to volume ratio.

Magnetic nanomaterials have attracted attention due to their potential applications as high-density magnetic recording media, catalysts, and microwave absorbers. In the biomedical field, they are used in targeted drug delivery system, as biosensors in cancer treatment methods, and even in magnetic resonance imaging [4, 5].

There are several techniques used for producing nanomaterials. To prepare SNF, various synthesizing methods have been reported, including *in situ* precipitation method, high-energy ball milling, reduction roasting, hydrothermal technique, advanced combustion route, co-precipitation, solvo thermal method, ultrasonic cavitations, microwave-assisted synthesis, thermal plasma, micro-emulsion method, combustion front quenching method, sol-gel auto combustion method, chemical precipitation method, self-propagating low-temperature combustion method, auto combustion technique, and traditional method, etc. [6,7]. However, some of the above methods faced problems like non-uniform particle size and containing impurities, which impose further advancement in the achievement of the products. The present trend in nanotechnology is to improve the synthesis methods of nanoparticles to make them more efficient, simple, clean, and eco-friendly. The synthesis of nanoparticles via "green" approach allows for obtaining nanoparticles with specified sizes and improved morphology. Green" synthesis prevents pollution during initial stages of chemical processes. These new "green" technologies can radically reduce environmental pollution and risk to human health. [8, 9].

Green syntheses of nanoparticles also provide advantages over other methods, as they are simple, single-step, cost-effective, eco-friendly and relatively reproducible and often results in more stable materials [10, 11]. The techniques for obtaining nanoparticles using naturally occurring reagents such as sugars, biodegradable polymers, plant extracts, and micro-organisms as reducing and capping agents can be considered attractive for nanotechnology[12, 13]. Recently, plant extracts of marigold flower, *Abutilon indium, Solanum tricobatum, Ziziphora tenuior,* Indian coral, mango steen, beetroot, *Ocimum tenuiflorum*, olive, Malabar neem, chamomile, clove extract, etc were used for the synthesis of NPs [14]. *Moringa oleifera* plant contain several phytochemical compounds in its natural extract such as retinol, niacin, gallic acid, ellagic acid, myricetin, chlorogenic acid, caffeic acid etc. [15-16].

In the present study we prepare $Cu_xZn_{1-x}Fe_2O_4$ (where x= 0.6 and 0.7) by the means of green route synthesis. We use moringa extract as a reducing, capping, stabilizing agent due to its easy availability and unique properties.

EXPERIMENTAL SETUP

Materials:

All of the chemical reagents were of analytical grade and were used without further purification before use. Distilled water was used as a solvent. *Moringa oleifera* extract was used as reducing, capping and stabilizing agent.

Plant collection and identification:

Moringa oleifera is also known as drumstick tree or *sahjan* tree (in Hindi). Height of tree is 10 – 12 m. Diameter ranges to ~45 cm, Young shoots are purplish (or) greenish white. It is usually grown in arid, semi-arid, tropical and sub-tropical region. For the present study plant leaves were collected from Mewar University campus, Chittorgarh which lies in between 25°01'58.6"N and 74°38'08.7"E and brought to the laboratory for further processing. Figure 1.1 shows the *Moringa oleifera* tree.

Identification: *Moringa oleifera* plant identification was done by the Department of Life Science of Mewar University, Chittorgarh.

Figure1.1: picture of *Moringa oleifera* tree

Preparation of Plant Extract:

For the preparation of leaf extract, fresh leaves were collected in a beaker and washed several times with water to remove the dust and finally with double distilled water. 10 g washed leaves were crushed in 100 ml double distilled water. After grinding the aqueous extract was taken in 250 ml beaker and boiled for 10 min at 80ºC temperature. The plant extract was allowed to cool at room temperature and then filtered with filter paper. The extract was collected and stored at 4ºC. This extract was used as a stabilizing, capping and reducing agents [17]. Figure 1.2 shows the flow chart of preparation of *MOE* as below-

Figure1.2: flow chart of preparation of *Moringa oleifera* extract

Preparation of $Cu_xZn_{1-X}Fe_2O_4$ (x =0.6 and 0.7) Nanoparticles:

For preparing the $Cu_xZn_{1-x}Fe_2O_4$ (x=0.6 and 0.7) nanoparticles, ratio of Copper sulphate penta- hydrate ($CuSO_4.5H_2O$) (0.1N), Zinc sulphate hepta- hydrate ($ZnSO_4.7H_2O$) (0.1N) and Ferrous sulphate hepta- hydrate ($FeSO_4.7H_2O$) (0.1N) were calculated and fixed as given in the Table1.

Table 1: Concentration of Chemical to Obtained Final Product

Sample	$CuSO4.5H_2O$ (ml)	$ZnSO_4.7H_2O$ (ml)	$FeSO_4.7H_2O$ (ml)	MOE (ml)
1(x=0.6)	80	53.3	266.7	80
2(x=0.7)	93.3	40	266.7	80

In the next step the precursors as prescribed in the above table were mixed with continued stirring at temperature 80ºC for 20-30 minutes. After that MOE was introduced in the solution as a capping and reducing agent. 20 ml of NaOH (0.1N) drop by drop was introduced into the solution to maintain the pH of the solution. Then precipitate was separated with filter paper.

Purification of Cu doped Zinc ferrites nanoparticles:

For further purification of filtered samples were washed with distilled water and air dried. To remove volatile impurities samples were heated at 150ºC in an oven for 4 hours. After that, samples were grinded and sintered at 400ºC for 4 hours.

Samples were again grinded to make fine powder and further characterization was done to confirm the nano range of the extracted samples.

Characterization of Cu -doped Zinc nano ferrites:

X- Ray Diffraction Analysis: X-ray diffraction is one of the analytical techniques used for materials characterization. XRD patterns were recorded on Philips PW 3050/10 model. The sample was recorded on a Philips X-Pert MMP diffractometer. The diffractometer was controlled and operated by a PC computer with the programs profit and used a CuKα (source with wavelength 1.5406 A◦, operating with Mo-tube radiation at 50 kV and 40 mA).

Results and Discussions

X- Ray Diffraction: $Cu_xZn_{1-X}Fe_2O_4$ (x =0.6 and 0.7) nanoparticles has been prepared by green route synthesis using MO plant extract. Obtained nanoparticles were characterized by X-ray diffractometer (XRD) in the range of 20–80º with a scanning step of 0.05º. Figure 2 shows XRD diffraction patterns for sample a) $Cu_{0.6}Zn_{0.4}Fe_2O_4$ and (b) $Cu_{0.7}Zn_{0.3}Fe_2O_4$.

To determine the particle size and phase morphology of prepared ferrite samples, XRD technique was used with angle 2Θ range 20º C - 80º C. Particle size of the ferrite samples calculated by the help of Scherer's equation [19]

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

D- Particle size (nm) (grain size)

K- Dimension less shape factor - 0.94

λ – X-ray wavelength of Cu kα radiation of the source which is 1.51418Å

β – Full wave half maxima (FWHM)

Θ- Bragg's angle (in radian)

Dislocation density (δ) = $\frac{1}{D^2}$ (2)

Strain (ε) = $\frac{\beta}{4tan\theta}$ (3)

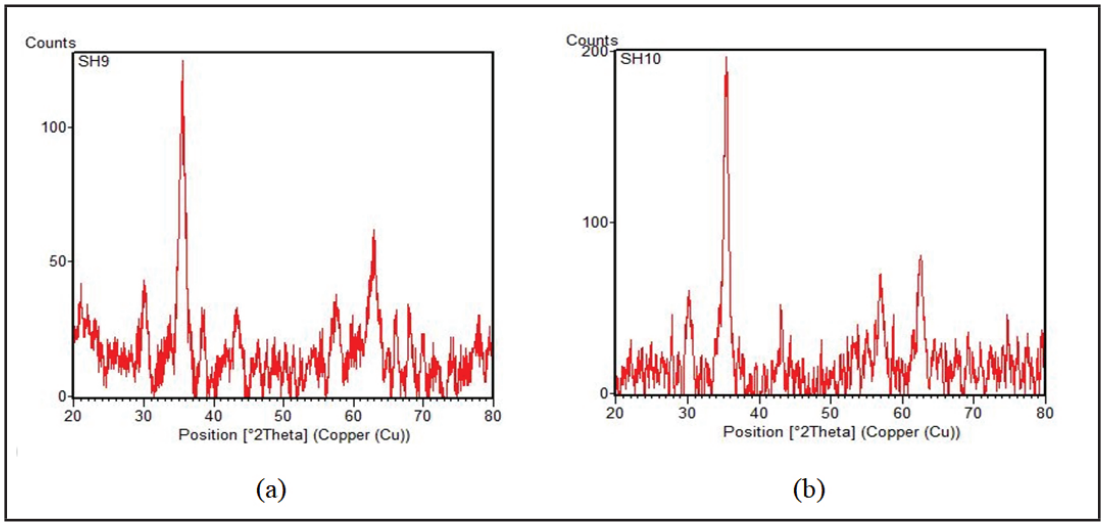

Figure 2: XRD diagram (a) $Cu_{0.6}Zn_{0.4}Fe_2O_4$ and (b) $Cu_{0.7}Zn_{0.3}Fe_2O_4$

As shown in the XRD diagram above (Fig-2), peaks were well defined and smooth. This shows that both the sample [$Cu_{0.6}Zn_{0.4}Fe_2O_4$ (Fig 2(a)) and $Cu_{0.7}Zn_{0.}3Fe_2O_4$ (Fig1 (b)] were crystalline in nature.

By the help of Scherrer equation [19] particle size (D), dislocation density (δ) and strain (ε) were calculated for both samples ($Cu_{0.6}Zn_{0.4}Fe_2O_4$ and $Cu_{0.7}Zn_{0.}3Fe_2O_4$) which are represented in the Table 2.1 and 2.2 respectively.

Table 2.1: XRD data analysis of $Cu_{0.6}Zn_{0.4}Fe_2O_4$

S. N.	2Θ (radian)	FWHM (radian)	D(nm)	Dislocation Density	Strain
1.	30.2828	0.944	9.114386	0.012038	0.015222
2.	35.63	0.629	13.86891	0.05199	0.008541
3.	43.48541	0.6297	14.19926	0.00496	0.00689
4.	65.995	0.47232	20.96475	0.002275	0.003174

Table 2.2: XRD data analysis of $Cu_{0.7}Zn_{0.3}Fe_2O_4$

S. N.	2Θ	FWHM	D(nm)	DISSLOCATION DENSITY	STRAIN
	30.258	0.7872	10.92921	0.008372	0.012705
	35.45	0.6297	13.84652	0.005216	0.008596
	43.0712	0.6296	14.18117	0.004973	0.006961
	56.94	0.6297	15.00316	0.004443	0.005067
	62.4	0.697	15.41873	0.004206	0.004537

Table 2.1 and 2.2 shows the XRD data analysis of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ and $Cu_{0.7}Zn_{0.3}Fe_2O_4$ respectively. Calculation shows that the samples are in nano range. Table 2.1 signifies that the particle size of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ sample is in the range of 9.11nm to 20.96nm .In Table 2.2 particle size of $Cu_{0.7}Zn_{0.3}Fe_2O_4$ sample is in range of 10.92 nm to 15.41nm is identified and calculated. XRD data analysis shows that as particle size increases dislocation density. It signifies that strength of material increases[19].

The result clearly shows that both the sample were in the nano range and crystalline in nature.

CONCLUSION

$Cu_{0.6}Zn_{0.4}Fe_2O_4$ and $Cu_{0.7}Zn_{0.3}Fe_2O_4$ SNF were successfully prepared by the help of green route synthesis method. XRD data shows that the average particle size of prepared nanoparticles was in nanometer range. The particle size of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ sample was 9.11nm-20.96nm and for $Cu_{0.7}Zn_{0.3}Fe_2O_4$ sample particle size was 10.92nm-15.41nm. .This study shows that the green route synthesis of ferrites nanoparticles allows not only obtaining the nanoparticles but also it enhances the structural properties of the material. It is very easy technique with low cost and efficient with no harmful effect on the environment.

The nanoparticles obtained using this technology are having applications in optoelectronic, photo catalytic and pharmaceutical fields. Cu doped Zn nano ferrites find application in designing transformers, transducers, and inductors. Ferrites are also used in magnetic fluids, sensors, and biosensors. Cu doped Zinc ferrites are also used in EM wave absorber, in MRI systems. Apart from these advantages, they play a vital role in practical appliances like mobile, laptops, mobile chargers, refrigerators, washing machines, microwave ovens, printers, and so on.

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