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THERMAL PROPERTIES OF PSS COATED COBALT ZINC FERRITE NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION METHOD

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In this work Cobalt Zinc Ferrite nanoparticles $Co_{1-x}Zn_xFe_2O_4$ for x = 0.25, 0.5 and 0.75 were synthesized via coprecipitation method. Annealing of all the samples was carried out at 700 ^oC for 5 hours. To investigate the crystal structure XRD analysis was used which confirmed the ferrite structure of synthesized samples. Afterwards surface coating of all the samples was done by biocompatible polymer PSS. Surface functionalization of magnetic nanoparticles with PSS (Polystyrene Sulphonate) was confirmed by FTIR spectrum of samples from 2000 cm^{-1} to 4000 cm^{-1}. Thermal properties and temperature variation with oscillating magnetic field was investigated by RF induction method. That showed increasing temperatures with decreasing concentration of Zinc content.Also Increase in temperature was observed directly related to the frequency of applied magnetic field and concentration of Cobalt in the sample. SAR values for the sample were estimated using specific heat of samples and temperature slope and it was observed that SAR is directly related to cobalt content as well as inversely to the Zn content in the samples.

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Keywords: Hyperthermia, Co-precipitation Method, Polymer coating PSS, Thermal properties

1. Introduction

At present nanoparticles have large number of applications in medical and electronics and many more fields. Importance of nanoparticle having magnetic properties has grown even more in the recent years to improve the applicability, it has been focused by many of researcher to enhance magnetic and thermal properties of these magnetic nanoparticles such as for hyperthermia applications. Investigating ferrite nanoparticles remained keen interest for observers because of their enhanced magneto-thermal properties [1-2]. Due to magnetic and thermal properties as hyperthermia cancer therapy bio imaging, MRI, delivering drugs to some specific parts of body, biosensing and many more depend on the magnetic and magneto-thermal properties such as super Para magnetism of the magnetic nanoparticles [3-5]. Magnetic nanoparticles showed considerable electrical, optical and magneto thermal properties. A general formula for Spinel ferrite is XFe_2O_4 where X = Co, Ni, Zn, Mn, Cu, etc. These ferrites are used different fields, such as biomedical, electronic circuits information systems, energy storing devices and ferrofluid [6-9].

Numerous methods have been employed for synthesizing ferrite particles such as auto combustion/microwave method, sol--gel, chemical co-precipitation, and solid-state method. [10-13]. In previous researches $CoFe_2O_4$ nanoparticles has been prepared with some enhanced dispersion properties implying hydrothermal technique [14]. PVA coated $Ni_{0.3}Zn_{0.7}Fe_2O_4$ nanoparticles were successfully prepared by M. Rahimi et, al. via sol-gel synthesis with a particle size from 17 to 20 nm [15]. Rautet. al. produced Zn doped $CoFe_2O_4$ nanoparticles using sol gel synthesis and prepared particle up to 45-49 nm in size [16]. Due to good magnetic properties cobalt-ferrite can be considered as a good candidate for biomedical and industrial applications. It has large coerciveness, larger coefficients for magnetostriction, and moderate saturation magnetization. Structure of $CoFe_2O_4$ is inverse spinel but it attains normal spinal structure by substitutions ions like Zn, Ni and Cd. [17]. Magnetic hardness of Cobalt-ferrite can be decreased by doping of Zn. Transition from ferromagnetic behavior to superparamagnetic properties can be achieved by Zn doping in Co-ferrites [18].

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Cobalt-Zinc ferrites nanoparticles of size 11 to 28 nm has also been synthesized by Ben Ali et, al using sol gel synthesis [19]. As compare to other methods, the co-precipitation is a method that can be comprehensively used for the preparing spinal ferrite nanoparticles because it is easy, low cost and practically reliable. [20]. Using Co-precipitation technique, we can produce a uniform powder in an easy way having no extra fuel requirements as citrus extract etc.

$Co_{1-x}Zn_xFe_2O_4$ nanoparticles are synthesized with (x = 0.25, 0.5 and 0.75) by Co precipitation and annealed at 700 ^oC for 5 hours. Synthesized MNPs were coated by polymer (PSS). Our research was aimed to study thermal properties of PSS Coated $Co_{1-x}Zn_xFe_2O_4$. Co-Zn ferrite nanoparticles were characterized by XRD, FTIR, RF induction heating to examine thermal properties of synthesized material. SAR values were calculated and compared with respect to Zn content in the samples as well as with the frequency of applied magnetic field.

Due to enormous potential of ferrites applications at high frequencies, their high resistance for corrosion, less prices, their enhanced properties such as high magneto crystalline anisotropy, good SAR values and higher sensitivities in MRI makes Co-Zn ferrite a promising candidate to be studied for further improvements and innovations. This study is aimed to explore thermal properties of Co-Zn ferrite nanoparticles as well as to see the effects of coating of polymer (PSS) as this polymer coating is not being used for this ferrite yet. So it's a new polymer whose effects on thermal properties can be investigated.

2. Materials and methods

2.1. Materials and synthesis

$Co_{1-x}Zn_xFe_2O_4$ nanoparticles with doping concentration x as 0.25, 0.5 and 0.75 are prepared by the Co-precipitation method. Chemicals used includes analytical grade Cobalt-Chloride Hexahydrate ($CoCl_2.6H_2O$), Zinc-Chloride ($ZnCl_2$), Ferric Chloride ($FeCl_3$) and Sodium Hydroxide (NaOH). Aqueous solutions of $CoCl_2.6H_2O$, $ZnCl_2$, and $FeCl_3$ were prepared by adding stoichiometric amount of each chloride with distilled water. Then all solutions were mixed and added NaOH drop by drop to attain the PH value as 11. The mixture was stirred for half hour at room temperature. After that the solution heated to 80 °C on hot plate with magnetic stirring for two hours. Then solution was kept up to the time to cool down to room temperature. Then washed precipitates with doubly ionized water to remove impurities. The solution was then dried in oven at 150 ^oC for an hour to get fine powder nanoparticles. The nanoparticles synthesized were further annealed at 700 ^oC for 5 hours for each concentration and allowed to cool down to room temperature overnight. After that for surface coating of nanoparticles, 0.01% solution of PSS was made to be mixed with 20% solution of Co-Zn ferrite. Both solutions were mixed and stirred at 100 ^oC for one hour and the temp was raised to 120 for half hour. The solution was washed again 2 times with DI water while and one time with acetone. The solution was allowed to dry at room temp for 48 hours. As a result, fine powder of PSS coated Co1-xZnxFe2O4 nanoparticles were synthesized.

2.2. Characterization techniques

Study of structural properties of samples of $Co_{1-x}Zn_xFe_2O_4$ (x=0.25, 0.5 and 0.75,) was done by the X-ray diffraction (XRD). The samples in the powder form were characterized by X-ray with λ=1.5406Å radiation, operated 2θ range of 15° to 80°. FTIR spectra of all the samples between the wavenumber range 2000 cm^{-1} to 4000 cm^{-1}were studied to confirm surface functionalization of prepared nanoparticles at room temperature. Thermal properties were studied by RF induction heating at frequencies 108.9, 327.3, 518.7 KHz. and increase in temp was recorded with respect to time.

3. Results and discussions

3.1. X-Ray Diffraction (XRD)

Diffraction patterns obtained from XRD of the prepared samples of $Co_{1-x}Zn_xFe_2O_4$ with (X = 0.25, 0.5, 0.75) are given in Fig. 1. Cubic spinel structure is observed for all the samples corresponding to the pure cobalt Ferrite (JCPDS 22-1086) with a slight peak shifting due to Zn substitution. No additional peaks were observed. This shows proper substitution of Zn in cobalt ferrite matrix. (h k l) values as (220), (311), (400), (422), (511), and (440) shows the cubic spinel structure for all the samples [21]. The crystallite size of every single arranged example was determined by utilizing Debye-Scherrer's equation (1)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where crystallite size is D, λ is wavelength of X-ray, k is a constant having a value of 0.9, θ is diffraction angle can be obtained from 2θ and β is FWHM (full width at half maximum). Observed crystallite size of the Sample is found to be between 13 nm to 19 nm which increments with the grouping of zinc as shown in table 2.

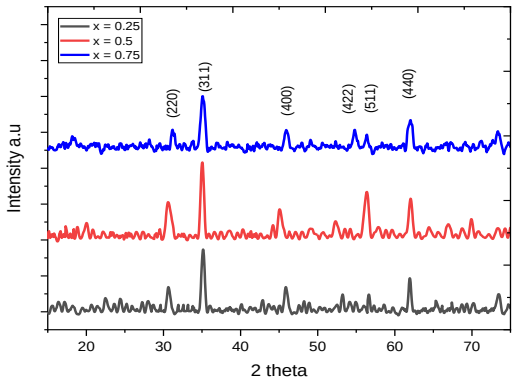

Fig. 1. X-Ray Diffraction (XRD) $Co_{1-x}Zn_xFe_2O_4$.

Table 1. XRD values.

x = 0.25						
Angle (2θ)	29.78	35.03	45.12	52.36	56.33	62.04
Planes (hkl)	220	311	400	422	511	440
D_{xrd} (nm)	13	19	16	16	13	16

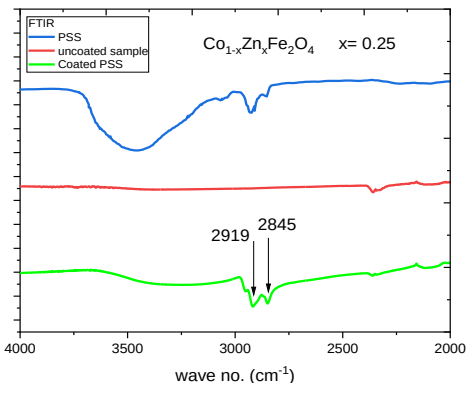

Fig. 2. FTIR curve of PSS, PSS coated and uncoated $Co_{1-x}Zn_xFe_2O_4$ (x = 0.25).

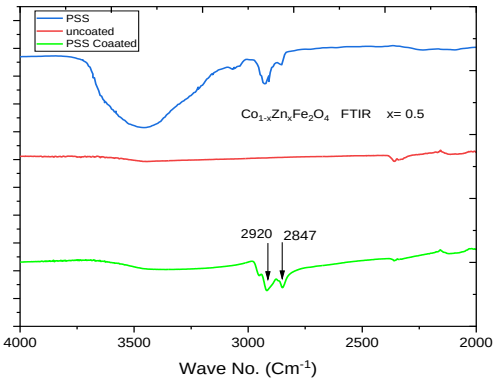

Fig. 3. FTIR curve of PSS, PSS coated and uncoated $Co_{1-x}Zn_xFe_2O_4$. (x = 0.5).

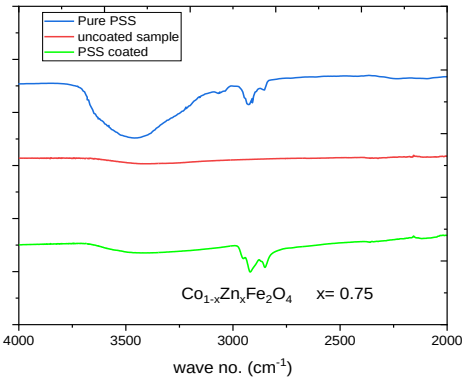

Fig. 4. FTIR curve of PSS, PSS coated and uncoated Co1-xZnxFe2O4. (x = 0.75).

3.3. RF Induction Heating

To measure the heating response of PSS Coated MNPs were exposed to oscillating magnetic field for RF induction heating. Temperature curves of samples were obtained are presented in fig. 5, 6 and 7 for the samples x= 0.25,0.5 and 0.75 respectively by applying an AC magnetic field of frequency 108.9kHz, 327.3 kHz and 518.7 kHz.

The results we observed from RF curves of samples are quite satisfactory for the use of prepared MNP for hyperthermia therapy, it is seen that as all samples responded very well for 327.3 and 518.7 kHz frequency, at these applied frequency particles attain the required therapeutic range (42-45 ^{o}C) just within few seconds as shown by the curves. The thermal response of all sample for frequencies shows that the temperature rises with respect to exposure time to oscillating magnetic field is directly proportional to the frequency under same insulating conditions. Fig. 8 and 9 shows the thermal response of the samples with respect to the doping concentration of Zn for the frequencies 327.3 kHz and 518.7 kHz. Which shows that samples having less Zn content show rapid and greater rise in temperature for the same conditions.

This depicts that $Co_{1-x}Zn_xFe_2O_4$ (x = 0.25) has more potential of achieving hyperthermia range in shorter time duration at high frequency than $Co_{1-x}Zn_xFe_2O_4$ (x = 0.5,0.75). Among all these samples the shortest duration for achieving hyperthermia temperature was observed for sample (x = 0.25) with PSS coatings which is just 7 sec, found to be the most quickly response giving mediator in the present study. Temperature rise with respect to 3 frequencies (108 kHz, 327 kHz and 518 kHz) of oscillating magnetic field is being plotted in the Figs. 5,6 and 7 for sample having x = 0.25, 0.5 and 0.75 respectively. It can be seen from these curves that rise in temperature is directly related with the applied frequency of magnetic field.

Figs. 8 and 9 shows a comparison of variation of temperature of three sample with same frequency which shows that rise in temperature of ferrite particles is inversely related to the Zn content in the samples. The samples having less Zn shows more temperature rise and final

temperature and vice versa. It can be concluded that the magnetic properties of samples are being suppressed with increase in the Zn concentration in the sample while increase in Co content increases the magnetic properties of sample and when these magnetic moment are flipped in presence of external filed they give rise in temperature.

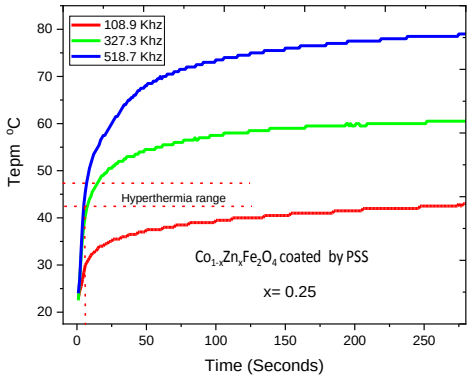

Fig. 5. RF Heating curve of Co1-xZnxFe2O4 by 3 frequencies (x= 0.25).

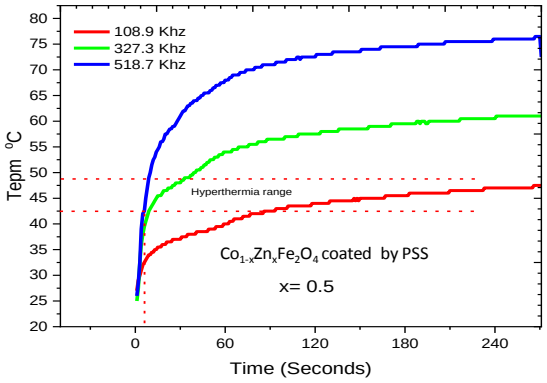

Fig. 6. RF Heating curve of Co1-xZnxFe2O4 by 3 frequencies (x= 0.5).

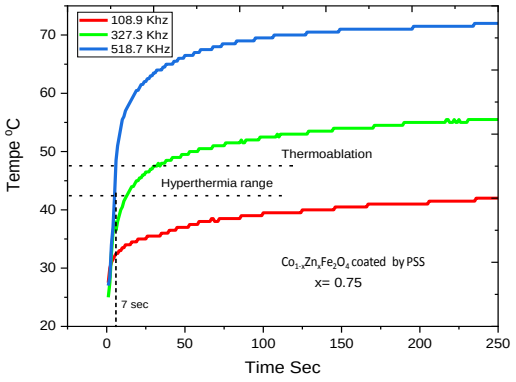

Fig. 7. RF Heating curve of Co1-xZnxFe2O4 by 3 frequencies (x= 0.75).

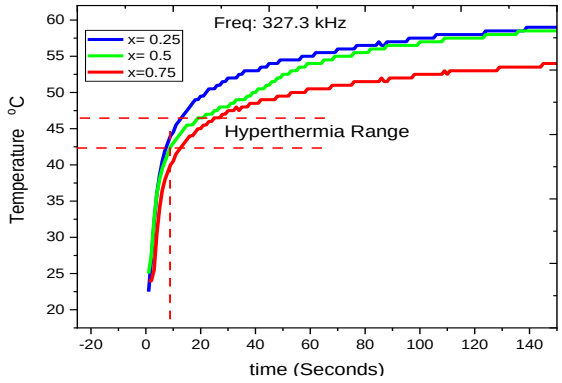

Fig. 8. RF Heating curve of Co1-xZnxFe2O4 at 327.7 kHz (x= 0.25 ,0.5, .75).

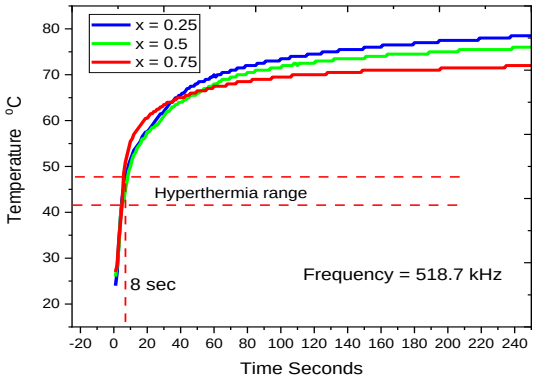

Fig. 9. RF Heating curve of Co1-xZnxFe2O4 at 518.7 kHz (x= 0.25 ,0.5, 0.75).

3.4. SAR values of Cobalt Zinc Ferrite Nanoparticles

Another important feature of MNPs for hyperthermia therapy is their SAR value It can be defined as the ability of MNPs to produce heat, that arises due to the interactions between magnetic moments of NPs and the external Oscillating magnetic field [41]. MNPs with high SAR values can be better candidate for bio-medical applications. To calculate SAR value, following formula is being used.

$$\text{SAR}=c\left(\frac{\Delta T}{\Delta t}\right)\frac{\textit{mass of sample}}{\textit{mass of Mag components}} \tag{2}$$

where c is specific heat for COZN NPs was found by using the law of mixtures of specific heat for the samples with all three concentrations (x = 0.25, 0.5, 0.75) as given in the table 2. mass of Magnetic components Co and Fe was calculated by using following formula.

$$\text{Mass of Mag components} = \frac{(\textbf{mass of sample})(\textbf{molar mass of Mn})}{\textbf{molar mass of Fe or Co}} \tag{3}$$

$\left(\frac{\Delta \mathbf{T}}{\Delta \mathbf{t}}\right)$ is slope of time-temperature curve of MNPs for initial 4 sec. This gives the spontaneous heating response of nanoparticles due to flipping of magnetic moments with Oscillating external magnetic field. MNPs with large value of initial slopes can be a good choice for hyperthermia treatment as their response will be spontaneous to AC field to attain the required temperature quickly.

Values of were calculated by manipulation of initial slopes of RF heating curves initial 4four seconds in presence of oscillating Magnetic field for frequencies 327.2 kHz and 518.7 kHz

as follows and the SAR values calculated are given in the table 2 and plotted in Fig. 10-11. Variation of SAR values for both frequencies 327 and 518 kHz are plotted in Fig. 12. Plot depicts that SAR value decreases with increase in Zn content as well as increases directly with increase in Co content and frequency of external magnetic field.

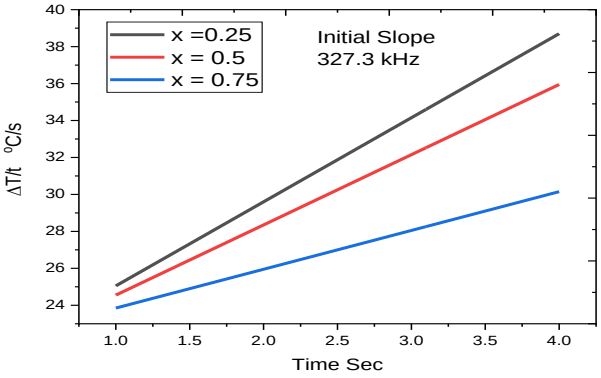

Fig. 10. Initial slopes of ΔT/t of three sample for Freq 327.3 kHz.

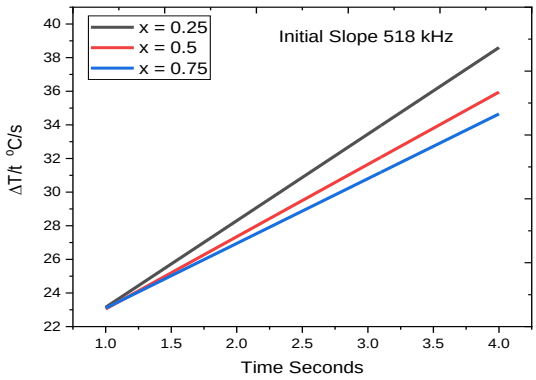

Fig. 11. Initial slopes of ΔT/t of three sample for Freq 518.7 kHz.

Table 2. SAR values of two samples.

Frequency kHz	**Sample Concentration**	**Final Temperature °C**	**SAR Value (W/g)**	**ΔT/Δt (℃/s)**
327.3 kHz	X = 0.25	60.5	4.02	4.68
	X= 0.5	61.5	3.9	4.12
	X = 0.75	56	2.88	2.72
518.7 kHz	X = 0.25	79.5	4.2	5.15
	X= 0.5	76.5	4.1	4.3
	X = 0.75	72	4.0	3.85

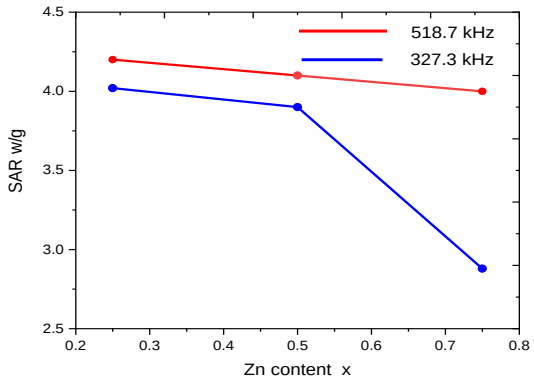

Fig. 12. Variation of SAR with Zn.

4. Conclusion

$Co_{1-x}Zn_xFe_2O_4$ ferrite nanoparticles with x value 0.25, 0.5, 0.75 were prepared successfully by co-precipitation method. These nanoparticles have ferrite spinel structure as observed by XRD analysis. It was observed that crystallite size increases with increase in Zn content in these samples.

In FTIR Spectrum two main absorption peaks were observed at 2921 cm^{-1} and 2847 cm^{-1}, which represents characteristic peaks of PSS that confirmed the polymer coating of the sample by PSS. It was observed through RF heating curves that the samples having less Zn content show larger final temperature as well as greater initial slopes of temperature change with respect to time. Contrary to this if Co content increases the sample become more magnetic and due to increase in magnetic moment rapid increase in temp by flipping of moments, was observed when placed in oscillating magnetic field. Rising trend in SAR was also observed with increase in Co content. It was also observed that SAR values of sample is decreased up to some extent due to coating of polymer as compared to uncoated sample in earlier researches. It was observed through variation in thermal properties that magnetic properties of Co-Zn ferrites decrease with increasing Concentration of $Zn^{2+.}$ These nanoparticles are suitable for magnetic hyperthermia devices and magnetic hyperthermia cancer treatment

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