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pH influenced synthesis and characterization of $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nano ferrite for energy storage and high frequency applications

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Abstract. A spinel nanocrystalline $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ was prepared using co-precipitation method maintaining pH -7,10 and 12. The pH influenced structural, spectroscopic and magnetic parameters were recorded by X-ray diffraction (XRD), FTIR and VSM. The crystallite size (31.12 nm to 45.32nm), lattice dimension (8.4175 Å to 8.4368 Å), strain (2.525×10^{-3} to 3.669×10^{-3}), dislocation density ($1.024 \times 10^{15} \text{1/m}^2$ to $4.867 \times 10^{15} \text{1/m}^2$) shows considerable structural enhancement due to pH variation. The Fe-O group analysis by FTIR within 400-600 cm^{-1} corresponds to tetrahedral (587 cm^{-1} to 591 cm^{-1}) and octahedral (442 cm^{-1} to 444 cm^{-1}) vibration confirms the formation of spinel nanoferrites. The smooth hysteresis M-H loop with coercivity (12.5826 Oe to 11.2212 Oe), magnetic saturation (62.8431 emu/g to 66.2495 emu/g) and retentivity (0.6375 emu/g to 0.6988 emu/g) describes multi domain nature of prepared material. The obtained structural and magnetic parameter clearly indicates energy storage and high frequency application.

1. Introduction

A development of soft magnetic material in nanoscale shows wide applications in science and technology due to its tuneable structural, electrical and magnetic properties. The spinel ferrite is one of the categories of soft magnetic material represented with formula MFe_2O_4 , where M corresponds divalent metal ions located at tetrahedral site and Fe^{3+} at octahedral site respectively[1]. Depending on choice of divalent metal ions, synthesis method, heating treatment, pH, researchers shows the usefulness of spinel ferrite in high frequency application[2], memory devices[3], waste water treatment[4], environment and energy field application [5] and medical applications[6]. One of multimetal combination NiCuZn spinel ferrite shows remarkable electromagnetic properties in high frequency ranges makes them suitable for MLCIs applications. The miniaturisation of energy storage appliances makes considerable use of multilayer chip inductors (MLCIs). The enhanced magnetic properties of nanoferrites are necessary for effective MLCIs to reduce volume of ferrite in the chip, which is a requirement for video cameras, cell phones, and notebook computers that use MLCIs as critical



components. Thus, the development of superior NiCuZn ferrite has attracted widespread interest as essential component downsizing progresses [7].

It is previously reported that the synthesis method can modify structural and magnetic parameters of spinel ferrite. Therefore, in present paper, $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nano ferrite were prepared using co-precipitation route with pH variation. The pH accordance structural, spectroscopic and magnetic parameters were studied by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), vibrating sample magnetometer (VSM) techniques and obtained results are presented in this report.

2. Synthesis of Materials and Characterization tools

The $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ spinel nanoferrites was prepared using the coprecipitation method. A 0.4 Molar (0.4M) solution of Iron chloride (III) FeCl_3 and another 0.2 M of Nickel Chloride (II) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Copper Chloride (II) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and Zinc Chloride (II) ZnCl_2 were taken separately in 40 ml of double distilled water followed by stirring about 20 min to obtain homogeneous solution. After that, both divalent and trivalent solutions mixed together, heat at 80°C and stir continuously with the addition of NaOH (4M) to obtain a brown solution at pH-7. The resultant solution of NiCuZn was filtered by double distilled water and acetone 3-5 times and dried $\sim 100^\circ\text{C}$ for 2 h in an oven. The dried material was grind for 3 h using mortar and pestle. The same procedure was use for sample at pH-10 and pH-12. The obtained material was calcinated at 800°C for 5 h, grind for 1h to get fine powder form for structural, spectroscopic and magnetic investigation. The final samples of NiCuZn were coded as P-7, P-10 and P-12 in accordance with the pH values of 7, 10, and 12 respectively.

The structural analysis of P-7, P-10, and P-12 were recorded by X-Ray diffractometer (Rigaku Mini-Flex 600 Rigaku Japan) ($\lambda=1.5406 \text{ \AA}$). The Fe-O functional group analysis was recorded by Fourier Transform Infrared Spectroscopy (FTIR) within 400 cm^{-1} to 4000 cm^{-1} using (Model: Spectrum 400 FT-IR/FIR Spectrometer, Perkin Elmer, USA). The magnetic properties of prepared material were investigated using a M-H loop by Vibrating Sample Magnetometer (VSM) (7400 series Lakeshore).

3. Results and Discussion

3.1 X-ray diffraction analysis

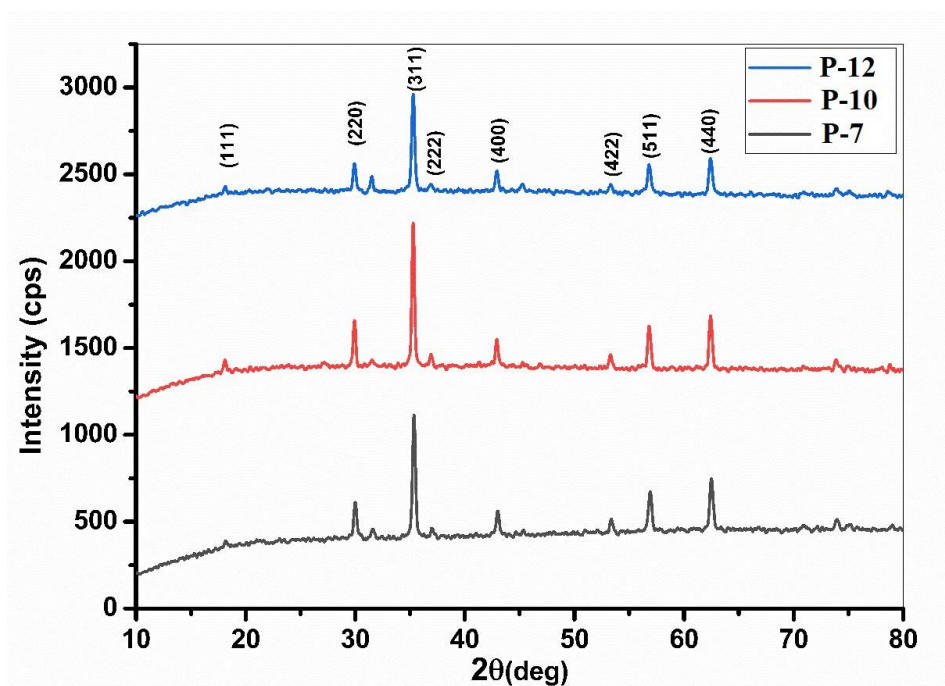


Figure 1. X-ray diffraction pattern of P-7, P-10 and P-12 nano ferrite.

The X-ray diffraction patterns of prepared $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nano ferrite (P-7, P-10 and P-12) are shown in Fig.1. The indexed diffraction plane of (111), (220), (311), (222), (400), (422), (511) and (440) at 2θ of 18.22° , 29.898° , 35.254° , 36.948° , 42.876° , 53.27° , 56.806° and 62.370° exhibits spinel structure of prepared material [8]. As shown in Fig.1, the appearance of strong (311) indicates magnificent crystallinity of all prepared material. However, the crystallinity for P-10 is higher than P-7 and P-12. The FWHM(β) related crystallite growth is almost constant for P-7 and P-12 than P-10. The reflection of 2θ and β on spinel structure are observed through crystallite size (D), dislocation density (δ), strain (ϵ), lattice dimension(a), bond lengths (d_{AX} and d_{BX}) and hopping lengths (d_{A} and d_{B}) computed for the most intense (311) peak and estimated in Table 1 and 2. [9]

From Table 1. The crystallite size for P-7 and P-12 was almost constant and lower compared to P-10 corresponds to the crystal growth at a faster rate than the nucleation growth for P-10 than that of P-7 and P-12 [10]. The lattice dimension(a) for P-10 shows higher value compared to P-7 and P-12 because of increased crystallization for P-10 compared to other two materials. The induced lattice strain (ϵ) for P-10 shows lower value compared to P-7 and P-12 mainly due to the broadening of diffraction peak recorded in diffraction pattern and dislocations in the prepared material. The obtain dislocation density(δ) shows higher value for P-10 compared to P-7 and P-12. The bond length at tetrahedral site(d_{AX}) and octahedral sites(d_{BX}) shows enhancement which attributed to cation distribution influenced by variation in pH. The magnetic ions distances (hopping lengths) on tetrahedral (d_{A})and octahedral(d_{B}) sites corresponds to potential require for charge carrier transfer from one cationic site to another. A quite larger d_{A} and d_{B} for P-10 signifies higher potential requirement in order to transfer charge carrier compared to P-7 and P-12 that will directly affect the dielectric properties of prepared material. The X-ray density ($\rho_{\text{X-ray}} = \frac{ZM}{N_{\text{A}}a^3}$) P-12 slightly higher than P-7 and P-10 signifies quit high number of pores present in the P-12 than other two material [11].

Overall enhanced structural parameters due to pH modifies spectroscopic and magnetic properties will be discussed further.

Table 1. Peak position (2θ), FWHM (β), Interplanar Spacing(d -spacing), Crystallite Size(D), Lattice dimension(a), Cell volume(V), Strain(ϵ) and Dislocation density(δ) of prepared P-7, P-10 and P-12 nano ferrite.

Samples	2θ (deg)	β (deg)	d - Spacing (Å)	D (nm)	a (Å)	V (cm^3)	ϵ (10^{-3})	δ (10^{15} 1/m^2)
P-7	35.336	0.268	2.5391	31.126	8.4175	596.416	3.669	1.032
P-10	35.254	0.184	2.5437	45.325	8.4368	600.463	2.525	4.867
P-12	35.263	0.267	2.5431	31.236	8.4345	600.036	3.663	1.024

Table 2. Bond lengths on tetrahedral and octahedral sites (d_{AX} and d_{BX}), Hopping lengths on tetrahedral and octahedral sites (d_{A} and d_{B}) and X-ray density($\rho_{\text{X-ray}}$) of prepared P-7, P-10 and P-12 nano ferrite.

Samples	d_{AX} (Å)	d_{BX} (Å)	d_{A} (Å)	d_{B} (Å)	$\rho_{\text{X-ray}}$ (g/cm^3)
P-7	1.952	2.026	3.644	2.975	5.311
P-10	1.957	2.031	3.653	2.982	5.275
P-12	1.956	2.031	3.652	2.981	5.279

3.2 Functional group analysis

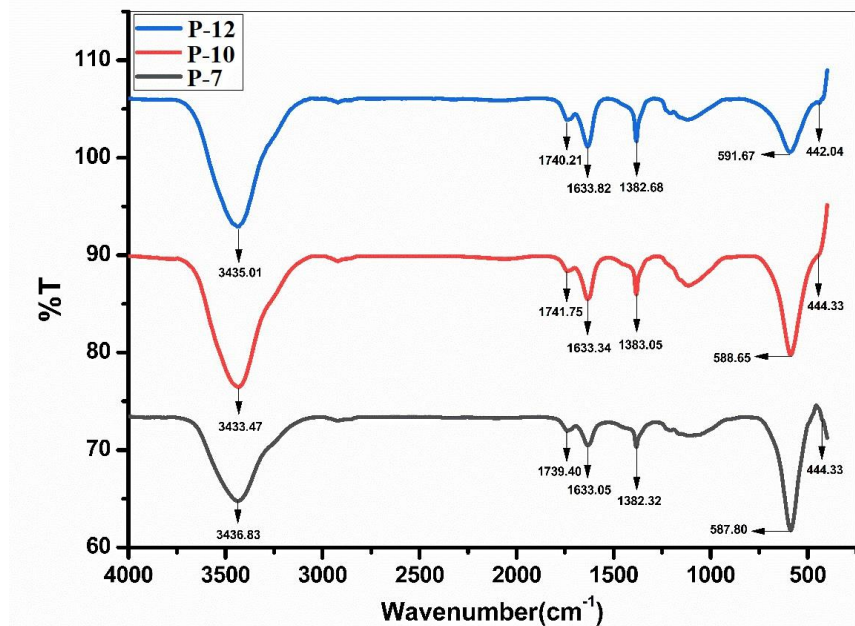


Figure 2. FTIR of prepared P-7, P-10 and P-12 nano ferrite

The functional group analysis by FTIR of prepared $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nano ferrite (P-7, P-10 and P-12) is shown in Fig. 2. The obtained FTIR spectra with relatively sharp peaks around 400 -600 cm^{-1} confirmed the formation of well-structured $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ spinel ferrites for all material [12]. For the prepared P-7, P-10 and P-12, the vibrational band at 591.67 cm^{-1} , 588.65 cm^{-1} and 587.80 cm^{-1} corresponds to tetrahedral metal oxygen stretching (ν_1) and 442.04 cm^{-1} , 444.33 cm^{-1} for octahedral metal oxygen stretching (ν_2) respectively (Table 3). From Table 3, the recorded ν_1 found to be decreases with pH variation attributed to enhanced bond length d_{AX} , whereas constant ν_2 for P-10 and P-12 is due to constant d_{BX} (see Table 2). From the recorded FTIR spectra, the strength of metal-oxygen bond at tetrahedral(A) and octahedral (B) sites can be describe using force constant at respective sites (K_{tetra} and K_{octa}) [13].

$$K = 4\pi^2 c^2 \nu^2 m$$

The obtained K_{tetra} and K_{octa} for P-7, P-10 and P-12 shows decreasing and saturated value, as the value of force constant solely depends on ν_1 and ν_2

Table 3. Tetrahedral vibration(ν_1), Octahedral vibration(ν_2), Force constant at tetrahedral and octahedral positions (K_{tetra} and K_{octa}), Average force constant (K_{av}) of prepared P-7, P-10 and P-12 nano ferrite.

Samples	ν_1 (cm^{-1})	ν_2 (cm^{-1})	K_{tetra} (N/m)	K_{octa} (N/m)	$K_{av}=(K_t+K_o)/2$
P-7	591.67	442.04	256.56	143.20	199.88
P-10	588.65	444.33	253.95	144.69	199.32
P-12	587.80	444.33	253.21	144.69	198.95

3.3 Magnetic Study

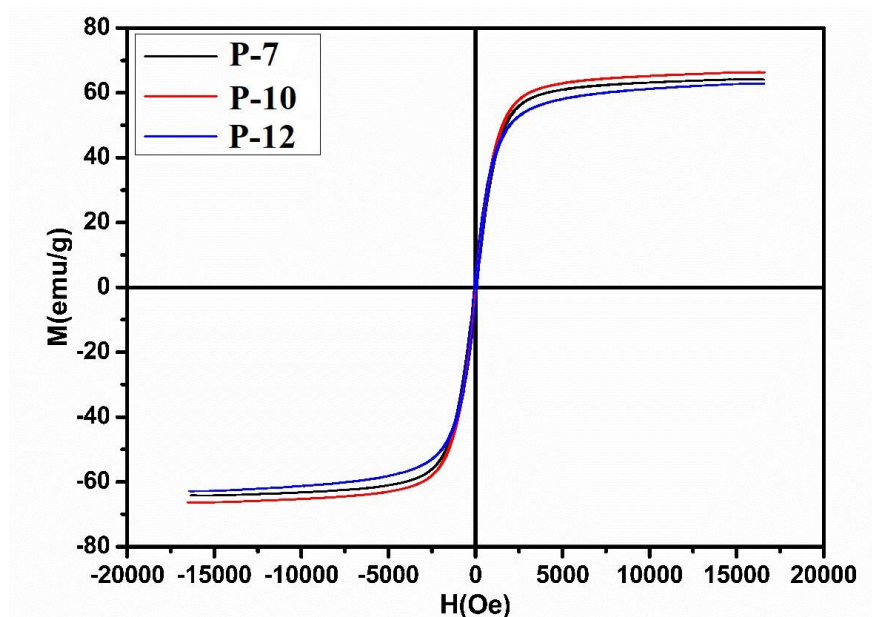


Figure 3. M-H loop of prepared P-7, P-10 and P-12 nanoferrite

The room temperature magnetic properties of prepared P-7, P-10 and P-12 was recorded by M-H loop (Figure 3). The smooth hysteresis M-H loop within ± 20 kOe corresponds to soft nature of prepared magnetic material. The magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) recorded from M-H loop are listed in Table 4.

As noticed from Table 4, The variation of pH in synthesis process modifies the magnetic parameters like M_s , M_r and H_c which alters the structural and magnetic properties as reported earlier [14]. The recorded lower M_s for higher pH-12 (P-12, 62.8431 emu/g) while moderated M_s (P-7, 64.0693 emu/g) for pH-7 and higher M_s for pH-10 (P-10, 66.2495 emu/g) attributed to rate of Fe^{3+} migration from tetrahedral(A) site to octahedral(B) site that increase or decrease net magnetization [15]. The decreasing behaviour of H_c from P-7 to P-12 (12.5826 Oe-11.2212 Oe) is a result of multidomain region and loss of anisotropy ($K = H_c M_s / 0.96$) due to the migration of cation to tetrahedral sites [16,17]. The observed squareness ratio (M_r/M_s) less than 0.05 signifies randomly oriented multi-domain nature of P-7, P-10 and P-12 [18]. It is important to note that smaller M_r/M_s is one of the particular requirement for ferrite in high frequency applications [19]. The recorded magnetic retentivity (M_r) was found to be lower for P-10 (0.6375 emu/g) compared to P-7 (0.6782) and P-12 (0.6988) because of the significantly lower strain (ϵ) of P-10 (2.525×10^{-3}) than P-7 (3.669×10^{-3}) and P-12 (3.663×10^{-3}) [20]. The obtained Bohr magneton (η_B (μ_B) = $M.M_s/5585$) was found to be increased for P-7 to P-10 and decreased for P-12 is mainly due to the nonlinear or canted spin ordering [21].

Table 4. Magnetic Saturation (M_s), Retentivity (M_r), Coercivity (H_c), Magneto-crystalline anisotropy (K), Bohr's magneton η_B (μ_B) and squareness ratio (M_r/M_s) of prepared P-7, P-10 and P-12 nano ferrite

Sample	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	K (erg/cm ³)	η_B (μ_B)	M_r/M_s
P-7	64.0693	0.6782	12.5826	839.7483	2.7361	0.010
P-10	66.2495	0.6375	12.1333	837.3177	2.8292	0.009
P-12	62.8431	0.6988	11.2212	734.5572	2.6837	0.011

4. Conclusions

A low temperature co-precipitation method was used to prepare $\text{Ni}_{0.3}\text{Cu}_{0.3}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nanoferrite at P-7, 10 and 12. The pH influenced structural, spectroscopic and magnetic properties of the prepared

material was recorded by X-ray diffraction, FTIR and VSM. Crystallite size (D), lattice dimension (a), strain(ϵ), and dislocation density(δ) showed changes in structural parameters as a result of the pH affecting nucleation growth and crystal growth. The Fe-O functional group analysis by FTIR in 400-600 cm^{-1} confirms the formation of spinel nanocrystalline material. The recorded (M_s , M_r and H_c) and computed (M_r/M_s) through VSM signifies multidomain nature of prepared nanoferrite which finds energy storage and high frequency applications.

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