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CHARACTERIZATION AND STUDIES OF MAGNETIC PROPERTIES OF NANO-CRYSTALLINE NICKEL ZINC FERRITES (NiZn-Fe_2O_4) SYNTHESIZED BY CALCINATION METHOD

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Nano crystalline form of nickel zinc ferrites (NiZn-Fe_2O_4) is prepared by high temperature calcination method at various proportion of Nickel and Zinc ions into the spinel structure of ferrites. The crystalline phase of as prepared NiZn-ferrites materials is characterized by XRD and TEM analysis. The magnetic properties of as prepared materials were analyzed by SQUID (superconducting quantum interface device) magnetometer. The broadening in XRD pattern due to nanoparticle formation in the crystalline phase of Ni-Zn-ferrites materials. TEM images are showing spherical and rectangular shapes of aggregated particle formation for Zn (0.6) Ni (0.4) Fe (2.0) $)_4$ composition.

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1. Introduction

Ferrites with nanoparticle size are recently emerged as important materials many applications such as magnetic recording media, magnetic micro fluids and nanofludic devices for the memory devices, magnetic resonance imaging technology, catalysis, magnetically acting drug delivery, gas sensors and in pigments [1-2]. The general formula of spinel (AB_2O_4)f errites is M-Fe_2O_3, where M is divalent ion transition metals such as Mn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, or Mg^{2+}. Modified nano-crystalline ferrites are having a great importance to studies their structural, magnetic and electronic properties and information technology for industrial applications [1-4]. Moreover, those cubic Ni–Zn ferrites are already proved as potential permeability at higher frequencies, high saturation magnetization (M_s), strong anisotropy and strong mechanical as well as chemical catalytic properties [7, 8].

Nickel and zinc incorporated ferrites have been prepared by many synthesis methods majority of which were by precipitation, sol-gel, microwave assisted heating and solid sate methods. Each preparation method has its own advantages to reduce the cost, consumption time and physic-chemical property alterations. Recently, nanoparticles of $Ni_xZn_{1-x}Fe_2O_4$ have been prepared by a chemical precipitation method [13-15]. The basic structural and physico-chemical property of the synthesized sample was characterized by XRD, FTIR and TEM analysis. The magnetic property with specific parameters such as M_s, H_c and M_r (magnetization Ms, remanence Mr, and coercively Hc) values depend on the nanoparticle size and composition of the synthesize strategy. The magnetic and structural morphology of Ni–Zn inverse spinel ferrite [$Zn_xNi_{(1-x)}$ Fe_2O_4, with varied composition of $x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1.0 is reported and

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the same prepared by ball milling method [16-20]. The XRD pattern of ball milled method prepared shows the spinel cubic phase with the present of magnetite phase present as impurity. The sample calcined at 1100 °C for 2 h results in the formation of pure spinel phase with improved particle size reduction.

Recently reported solvothermal route prepared Ni–Zn ferrites microspheres are synthesizing by solvo-thermal followed by calcination method are showing higher magnetic activity [21]. The calcination process is truly enhances the magnetic characteristics and M_s values becomes greater with Zn addition in the original precursors and it shows the highest value of 83.2 emu/g for $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Hence, in the present study, nanoparticles of as prepared NiZn ferrites are studied by SQUID method and further characterized by XRD and TEM techniques.

2. Experimental methods

2.1 Synthesis of NiZn-Ferrites samples

The chlorides of Ni, Zn and Fe were weighed using an electronic balance having an accuracy of 10^{-4} gram sensitivity and were mixed in appropriate proportion. The metal chlorides were dissolved in minimum volume of deionized water with constant stirring in an appropriate stoichiometric ratio. Then precipitating reagent were prepared by taking NaOH and Na_2CO_3 in the ratio 1:1. Precursor salts of Ni,Zn and Fe salt in 0.4 M HCl mixed with 1.5 M NaOH by drop wise addition. The precipitating reagent is added dropwise with constant mixing until co-precipitation occurs. Few ml of reagent is added in excess and left for some time to settle down the precipitate. The precipitates are filtered using suction pump. Precipitates were thoroughly washed with deionized water till free from sodium and chloride ions. The precipitate containing CO_3^{-2} and OH^- anions of metal is dried in an electric oven at a temp. 1100 ^oC for 24 hours and dried the obtained products followed by powdered in an agate mortar. Data of all samples were recorded by X-ray diffractometer from 5-75^o (2θ) at the rate of 5 s per step (Rigaku Geigerflex). CuKα radiation was generated at 35 kV and 15 mA. The dc magnetic analysis and hysteresis loop measurements (ca. area of $3 \times 3\ mm^2$ and thickness of ~100 μm) were performed from 2 to 300 K using a SQUID magnetometer (MPMS XL-7). FEI Tecnai G20 is used to recorded the Transmission electron micrographs (TEM).

3. Results and discussion

Fig. 1 indicated all $Ni_{1-x}Zn_xFe_2O_4$ (X(F1-F8)=0.2,0.4,0.6,0.8, 1.0,1.2,1.4,1.6) with respective XRD diffraction patterns of as prepared samples and it shows pure phase formation with cubic spinel ferrite structure. All peaks are indexed with respective *hkl* plan values such as (111), (220), (311), (222), (400), (422), and (511). The shift in the XRD peak position could be due to reduced particle size causes by ionic radii of the Zn2+ (0.83 Å) and the Ni2+ (0.78 Å) are different [15]. The XRD data were used to calculate the particle size (D), lattice parameter (a) etc,. Additionally, the average crystallite particle size for all prepared sample can be obtained by using using Scherrer's formula. Fig. 1. Shows the different amount of Ni and Zn incorporated ferrites nanocrystaline samples. The high temperature calcination method prepared NiZn ferrites cause huge broadening in XRD peaks at low angle due to formation nanoparticle formation for as prepared crystalline ferrites samples.

Table 1. Synthetic composition of Nickel Zinc Ferrite samples.

F1	Zn (0.25) Ni (0.75) Fe (2.0) O_4
F2	Zn (0) Ni (1) Fe (2.0)
F3	Zn (1) Ni (0) Fe (2.0)
F5	Zn (0.2) Ni (0.8) Fe (2.0)
F7	Zn (0.4) Ni (0.6) Fe (2.0)
F8	Zn (0.6) Ni (0.4) Fe (2.0)
	Zn (0.8) Ni (0.2) Fe (2.0)

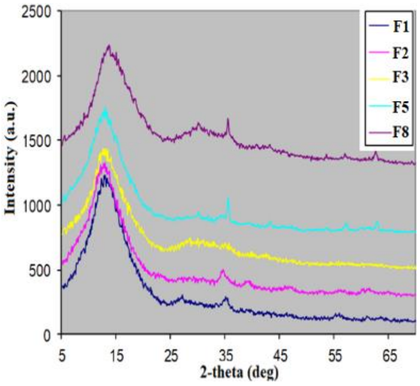

Fig. 1. XRD patterns various composition of NiZn-Ferrites samples.

Increasing in the concentration of Ni and Zn ion incorporation in ferrite lattice causing the addition XRD peak for samples like F5 and F8 in Fig. 1. The size of brooding is also increased for sample F8 due to formation of fine nanoparticles. Fig. 2 shows the comparative XRD pattern of NiZn and CuMgZn ferrites sample prepared by oil-in micro emulsion method of the reported data. The XRD patterns of our route prepared NiZn-Ferrite in Fig. 1 is more similar to the XRD peaks in Fig. 2 (first broadened spectra in XRD pattern).

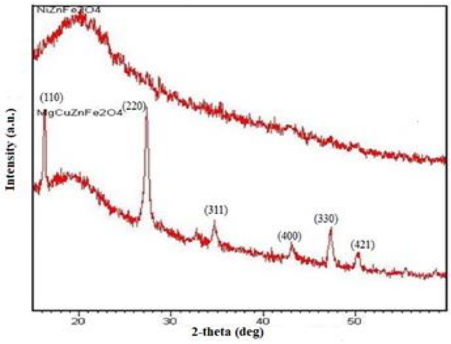

Fig. 2. Comparative XRD pattern of (a) MgCuZn-Ferrites and (b) NiZn-Ferrites [5].

Figs. 3 and 4 show the SQUID measurement of NiZn-ferrites samples with different composition of Ni and Zn incorporation into the ferrite spinel structure. ZFC (Zero field cooling) and FC (Field cooling) performance of the Nano ferrites materials with different composition as shown in Table 1 are presented in Fig. (3-5) for uncalcined and calcined samples. The meaning of calcination is treatment of sample at high temperature in air or inert atmosphere. In the present study, calcination of as prepared NiZn-ferrites samples are heat treatment carried out in tubular furnace at 600 ^{o}C in air. The as prepared sample is taken with known amount and studied its magnetic property by SQUID analysis.

Fig. 3 shows the SQUID measurement of samples were cooled down from 350 K to 50 K under ZF (zero fields) condition and magnetizations were recorded with increasing temperature by changing on with fixed magnetic field to get ZFC curves. For Field cooling (FC) measurements is also follow the same way like cooled down from 350 K to 50 K in presence of magnetic field.

From the Fig. 3 and 4 it shows that magnetization in the ZFC and FC curve decreases continuously with increasing temperature. However, in case of FC the magnetization always remains higher at lower temperatures and merges with ZFC values near and above blocking temperature (TB) [20-23]. Fig. 3 and 4 shows that the ZFC curve shows a curvature leading to a broad peak (sample F3, F8 and F9) only in the temperature range of 5 K to 50 K. The large width of peak is normally attributed to the varies size of particle distribution in the prepared ferrites. A wider peak observed for Nickel with the composition of 0.25 and 0.4 for two different samples compared to Ni=0.25 (F1) indicates that the formation of bigger particle size or a wider particle size distribution. Above blocking temperature (TB) all the particles are in the superparamagnetic state. The TB increases with increasing particle size due to known volume dependence of the magnetic particle with blocking temperature of a superparamagnetic system. The lowest TB and low peak broadening in Zero filed cooling (ZFC) curve obtained for F3,F9 and CF3,CF9. Temperature dependence of magnetization (ZFC and FC curves) of Nano ferrites $Ni_xZn_{1-x}Fe_2O_4$ (F3,F9 and CF3,CF9) (in lower temperature region) was represents the its smaller particle size or narrow size distribution [30]. Zero field cooled (ZFC) and field cooled (FC) response of magnetization as a function of temperature were measured and discussed in details.

From the Fig. 3 it concludes that the increasing amount of Zinc incorporation in ferrites samples is enhances the magnetic property of as prepared NiZn-ferrites samples. Optimized amount of Nickel addition is providing improved magnetic property compared higher amount of nickel addition in as prepared nano-ferrites samples. The amount of Nickel addition should below below X= 0.4, such as F8 and F9 composition.

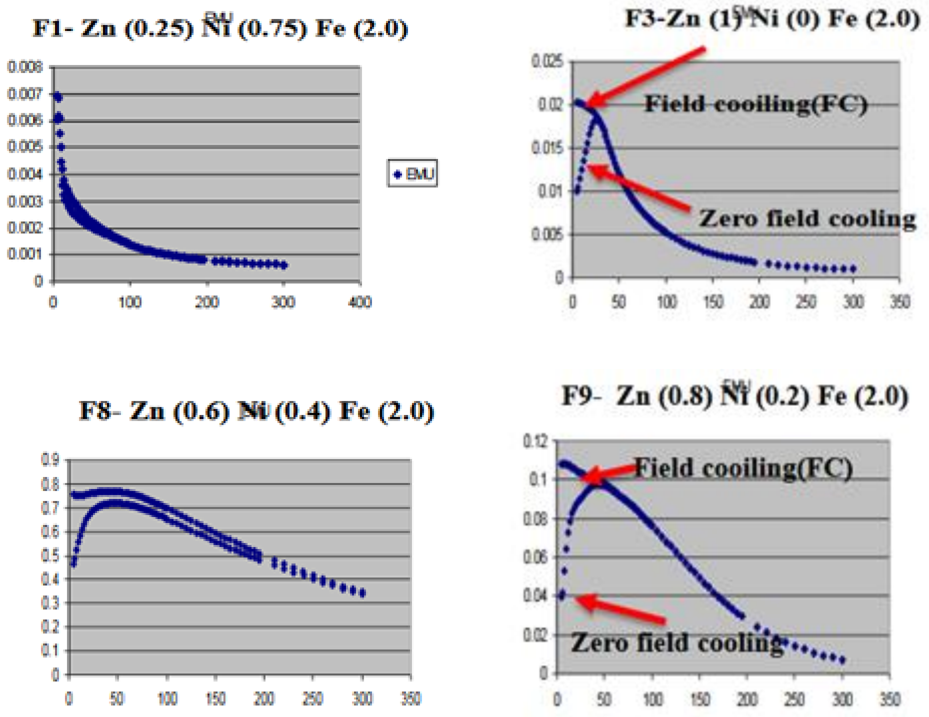

Fig. 3. SQUID magnetic emu measurements of NiZn-Ferrites (F1,F3, F8 and F9) samples.

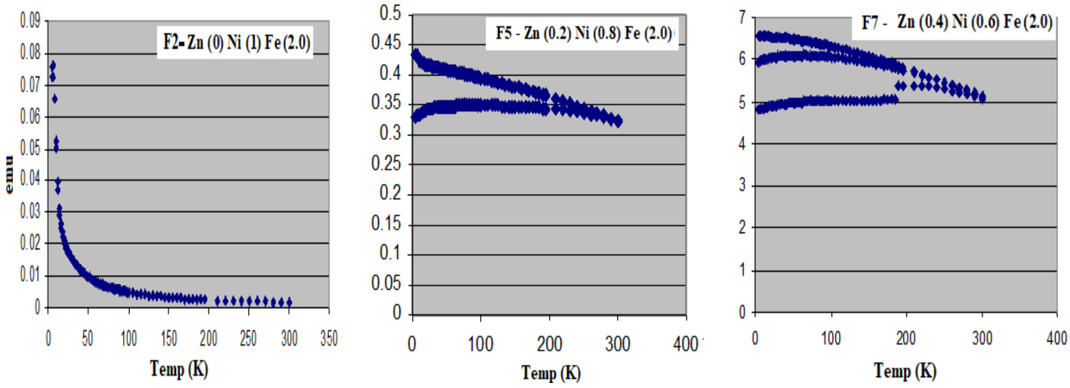

Fig. 4. SQUID magnetic emu measurements of NiZn-Ferrites (F2, F5 and F7) samples.

From Fig. 4, sample F7 shows much higher emu values for the respective NiZn-ferrites sample in presence of and absence of magnetic field compared to no zinc addition (F2) and less amount of Zinc addition (F5) samples.

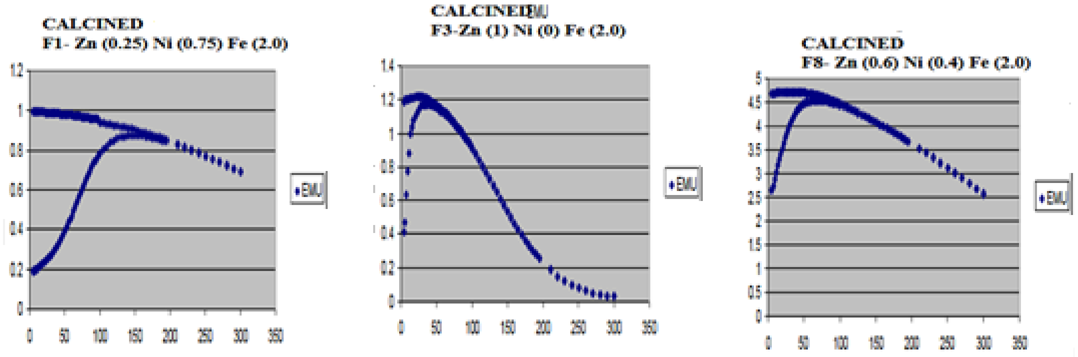

Fig. 5. SQUID magnetic emu measurements of Calcined NiZn-Ferrites (CF1,CF3 and CF8) samples.

Fig. 5 shows the magnetic property of calcined ferrites samples. After heat treatment of samples F1, F3 and F8 shows much improved magnetic emu values with typical narrow ZFC curves with lesser and wider blocking temperature. It concludes that the higher temperature heating or calcination process provide the enhanced emu values for sample CF8 sample. The strong anisotropy increases at low temperature and it results in higher magnetic saturation. Hence, the sample is cooled in the presence of magnetic field, results in changing in spin not happen. TEM images are shown in Fig. 6 (a-d), square and rectangle shaped aggregation particles obtained for (6a and 6b) for the synthesized F3 type NiZn-ferrites sample. The dark large particle aggregation due to presence of major content of iron oxide absorption with nickel and zinc meal ion incorporation (Fig 6c). Fig.6d shows the another places of NiZn ferrite dispersion and glassy morphology due Nickel and Zinc oxide formation with iron oxide surface.

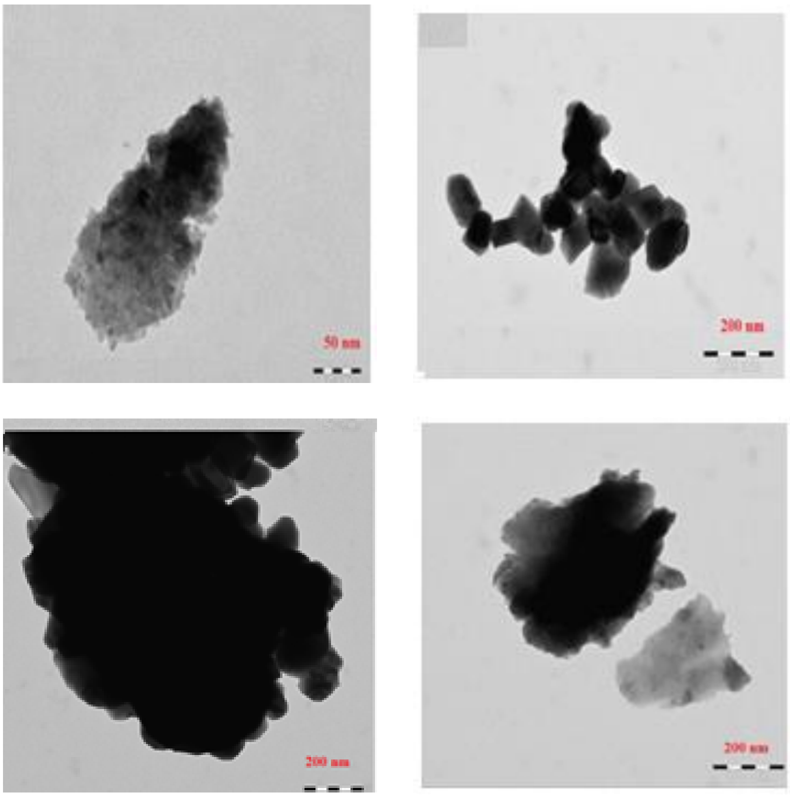

Fig. 6. (a-d) TEM images of CALCINED NiZn-Ferrites at different sites (F8- Zn (0.6) Ni (0.4) Fe (2.0)).

4. Conclusions

NiZn-ferrites nanocrysaline sample are prepared by precipitation and calcination method with nanoparticle formations. Magnetic properties are enhanced by optimized concentration of Nickel and Zinc addition into ferrites matrix. Nickel content between X= 0.4 to 0.8 is showing improved TB and emu values. Addition of Zinc with large amount enhances emu values for the synthesized ferrites samples. Square and rectangle shaped ferrites morphology obtained for our calcination route prepared samples. Hence, the prepared NiZn-Ferrites sample can be utilized for magnetic device applications.

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