

# Room Temperature Long Range Ferromagnetic Ordering in $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$ Nano magnetic System

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**Abstract.** The structural and magnetic behavior of sol-gel autocombustion synthesized nanocrystalline  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  have been investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), Mössbauer spectroscopy and vibrating sample magnetometer (VSM). Sample of high purity and high homogeneity was obtained by calcination at low temperature ( $500^\circ\text{C}$ ) resulting in nanoparticles of average diameter  $\sim 15\text{nm}$  as determined by XRD and further confirmed by TEM. X-ray diffraction (XRD) and selective area diffraction (SAED) confirmed the single phase of the sample. Mössbauer results are supported by magnetization data. Well defined sextets and appearance of hysteresis at room temperature indicate the existence of ferromagnetic coupling at room temperature finding material utility in magnetic storage data. The existence of iron in ferric state confirmed by isomer shift is a clear evidence of improved magnetic properties of the present system.

**Keywords:** Spinel ferrites, nano ferrites, HRTEM, magnetic properties, Mössbauer spectroscopy.

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## INTRODUCTION

Spinel ferrite nanoparticles are subject of immense interest due to their potential technological applications in field as varied as high frequency device components, soil remediation and medical diagnosis and treatments. Some of the novel properties of magnetic nanoparticles, such as superparamagnetism, quantum magnetic tunneling, and surface spin effects [1, 2] have generated further interest in the study of nanoparticles spinels. The common criteria for every application are the lowest magnetic loss due to which high resistivity is needed for these materials. In this regard Ni-Zn-ferrite is highly suited for their applications as soft magnetic materials because of low coercive field, high saturation magnetization, high Curie temperature, high-resistivity, chemical stability, lower power loss and low-production cost [3,4]. To carefully study and exploit the potential and possibilities associated with nanomaterials, the key point is to create well-defined, mono- disperse structures of predictable size, shape, crystallinity, and morphology through a straightforward synthesis. Thus, special interests have been paid to the synthesis technique that leads to formation and optimization of nanoferrites. In this context, sol-gel auto-combustion

method which we have opted offers various advantages over the conventional methods [5]. Further, in the nanocrystalline magnetic materials of Ni-Zn-ferrites, soft magnetic properties can be tailored by the addition of Co and Cu. The addition of Co enhances magnetic properties of NiZn ferrites, similarly Cu not only influences the magnetic properties but also influences the sintering temperature, ferrite density, etc. [6]. Further, few reports are available on Mössbauer investigations of nanocrystalline NiZn ferrites showing long range ferromagnetic ordering at room temperature with small particle size and low sintering temperature [7-9]. Ferromagnetic coupling is of great importance from technological application point of view. Mössbauer spectra for  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Fe}_2\text{O}_4$  nanoferrite at room temperature exhibit collective magnetic excitation [10]. The particular interest in the nanocrystalline  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  ferrite systems is due the achievement of room temperature long range ferromagnetic ordering with codoping of Co and Cu.

## EXPERIMENTAL

Nanocrystalline ferrite sample with composition  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  was prepared by the sol-

gel autocombustion method. The materials used were AR grade Nickel Nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], Zinc Nitrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], Copper Nitrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ], Cobalt Nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], Iron Nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ], Citric Acid [ $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ]. Stoichiometric proportions of the nitrate salts were taken for the preparation of nanoparticles. The prepared aqueous solution of nitrate salts and citric acid were mixed together with continuous stirring at room temperature. The molar ratio of nitrates to citric acid was maintained at 1: 1. Small amount of ammonia solution was added to bring the pH = 7. In a hot-wax container in contact with a hot plate, the water solution was left to evaporate at 80°C with continuous mechanical stirring, until a sticky gel was obtained. After gel formation, the beaker was put directly on hot plate at 150°C. The dried gel burnt in a self propagating combustion manner until all gel was completely burnt out to form a loose fluffy powder. The spontaneous combustion lasted for 20-30 s and gave rise to fluffy powdered product with glowing flints. The final powdered product was calcined at 500 °C for 5 h.

## RESULTS AND DISCUSSION

The X-ray powder diffraction pattern for  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite is presented in FIGURE 1. Inset of FIGURE 1, shows X-ray diffraction (XRD) patterns analysed with the help of *FullProf* programme by employing Rietveld refinement technique.

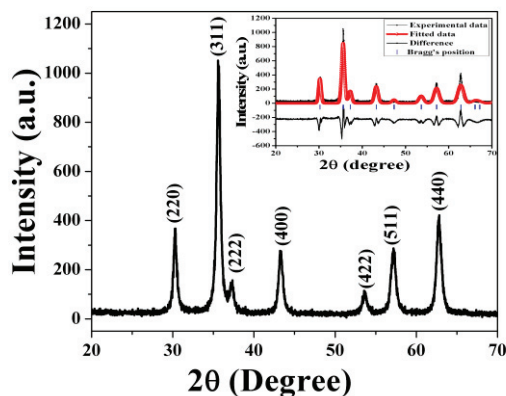


FIGURE 1. XRD analysis spectra of  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite

XRD refinement was continuous until convergence was reached with a goodness of fit index ( $\chi^2$ ) ~2.74. The peak position and relative intensity of all diffraction peaks match well with the standard powder diffraction file of JCPDS Card no. 08-0234 with Philips *X'pert HighScore* confirming the cubic spinel phase with Fd3m space group without any signature of

undesirable secondary phase. The average crystallite sizes of the ferrite calculated from the broadening of the (311) X-ray diffraction peak by the Debye-Scherrer equation was found to be ~15nm.

The representative illustration of TEM micrographs of synthesized nanoparticles are presented in FIGURE 2. An overview of the TEM image of nanoparticles shows that the nanoparticles are agglomerated. The agglomeration of particles may be because they experience a permanent magnetic moment proportional to their volume [11]. In the SAED image of synthesized particles, clearly visible distinct rings confirm good crystallinity of particles structure. The shape of the particles appears to be almost spherical. It has been observed that the size of the particles obtained through TEM measurement are in range 15-22 nm, corroborates well with the crystallite size obtained from XRD analysis.

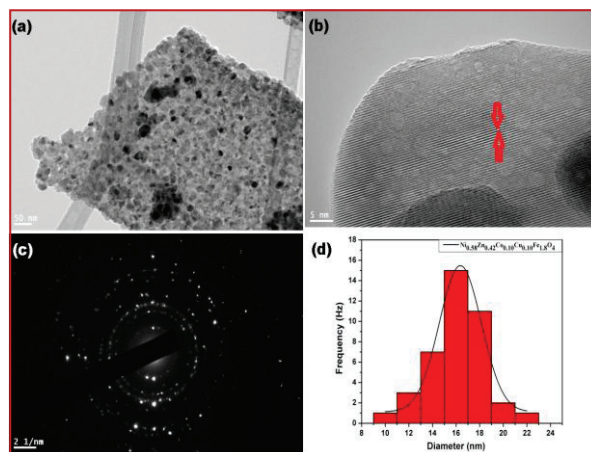
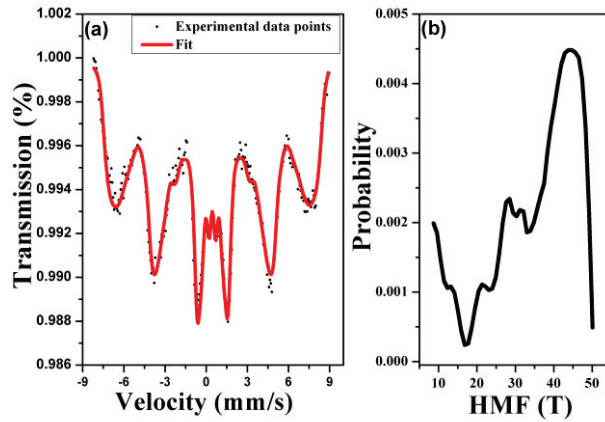


FIGURE 2. (a) Low resolution TEM, (b) HRTEM, (c) SAED pattern and (d) typical histogram showing size distribution of  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite

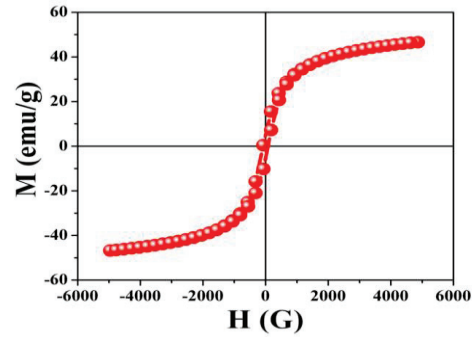
The room temperature  $^{57}\text{Fe}$  Mössbauer spectra for  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  (FIGURE 3(a)) show long range ferromagnetic ordering. In the observed typical spectra, the dots represent experimental data points and the solid lines represent the curve fitted results. The experimental data were fitted with least squares fitting programs *NORMOS-DIST*. The broad shape of spectral lines provides clear evidence of the wide distribution of magnetic field acting at the  $\text{Fe}^{3+}$  nuclei in the nanoparticles. FIGURE 3(b) shows the *p-B* distribution derived from the Mössbauer spectra of substituted NiZn nanoparticles. It can be seen that the spectrum has a wide range of Hyperfine Magnetic Field (HMF) field. Hyperfine distribution shows maximum near 44.54 T extending upto 50.69 T. The appearance of a doublet indicates presence of some superparamagnetic contribution imbedded in the long range ferromagnetic ordering which might be induced

by fine particle size effects. The doublet can only be observed when the superparamagnetic relaxation of the nanoparticles occurs at a rate faster than the Mössbauer measurement time, giving a time average zero magnetization. Consequently, the sextet peak and doublet peak can appear simultaneously. From spectra, it is evident that the material is perfectly magnetically ordered. The average value of isomer shift  $0.4584\text{mm/s}$  is consistent with high spin  $\text{Fe}^{3+}$  charge state [12]. Thus the results of Mössbauer study confirm the presence of  $\text{Fe}^{3+}$  ions in the sample and no signature of  $\text{Fe}^{2+}$  ions has been detected in the recorded Mössbauer spectra of the sample which results in the improved magnetic properties as confirmed by the room temperature M-H study, because in ferrites presence of  $\text{Fe}^{2+}$  deteriorate its magnetic properties.



**FIGURE 3.** (a) Mössbauer spectra and (b)  $p$ - $B$  distribution of  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite.

FIGURE 4. shows room temperature M-H curve of the samples at the field of 5000 Gauss. The saturation magnetization( $M_s$ ), coercivity( $H_c$ ), retentivity( $M_r$ ) and squareness ratio ( $M_r/M_s$ ) are  $46.60\text{emu/g}$ ,  $78.809\text{ Gauss}$ ,  $5.24\text{emu/g}$  and  $0.11$  respectively. The observation of hysteresis loops for prepared nanoferrite at the room temperature is consistent with the occurrence of a ferrimagnetic or a ferromagnetic ordering in these nanocrystals. The value of  $M_s$  is also interestingly high compared to the same reported for the substituted Ni-Zn-ferrite nanocrystalline system [10] which may be attributed to strong  $\text{Fe}_A^{3+}\text{-O-Fe}_B^{3+}$  superexchange interactions and cation distribution in present system.



**FIGURE 4.** Room temperature M-H curve of  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite

It is clear that room temperature magnetic behavior of  $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Co}_{0.10}\text{Cu}_{0.10}\text{Fe}_{1.8}\text{O}_4$  nanoferrite is consistent with Mössbauer measurements. Such a clearly defined hysteresis and well defined sextet at room temperature indicates that these nanoparticles are truly ferromagnetic.

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