

Synthesis and Mössbauer studies on Nickel-Zinc-Copper nanoferrites

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Abstract- Polycrystalline Ni-Zn ferrite, with a well-defined composition, $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, synthesized by a low temperature method showed the formation of a cubic ferrite phase with a crystallite size of ~ 15 nm and saturation magnetization of $M_s \approx 44$ emu/g at room temperature. When calcined at higher temperatures (up to 1200 °C) the magnetization increased continuously to $M_s \approx 67$ emu/g. To understand the magnetic nature of the cubic ferrite phase formed at a temperature as low as 80 °C, ^{57}Fe Mössbauer spectra were recorded for samples annealed at three different temperatures, without any external magnetic field, and with an external field of $H_{\text{ext}} = 5$ T, at 4.2 K. The spectral parameters at room temperature, namely, isomer shift, quadrupole splitting and hyperfine field, confirmed the presence of ultrafine superparamagnetic crystallites of Ni-Zn ferrite. The Mössbauer spectra at 4.2 K revealed spin relaxation effects resulting in very broad sextets, characteristic of ultrafine crystallites. The Mössbauer spectra recorded at 4.2 K and $H_{\text{ext}}=5\text{T}$ showed well-resolved two-sextet pattern with characteristic hyperfine interaction parameters of the cubic ferrite phase.

INTRODUCTION

Ferrite materials have been under intense research for so long due to their useful electromagnetic characteristics for a large number of applications [1]. The performance of these materials in their bulk form where the grain dimensions are in micrometer scales is limited to a few megahertz frequency due to their higher electrical conductivity and domain wall resonance [2, 3]. However, the recent technological advances in electronics industry demand even more compact cores for work at higher frequencies [4]. One way to solve this problem is by synthesizing the ferrite particles in nanometric scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multidomain formation, the particle is in a single domain state. Domain wall resonance is avoided, and the material can work at higher frequencies.

Nanoferrites can be produced by a number of ways such as coprecipitation of hydroxide [5], sol-gel method [6], hydrothermal [7] and mechano synthesis

approach of ball milling [8] etc. It is not sure that whether the different methods produce the same microstructure but this paper reports the results of coprecipitation as this method provide good control over the particle size and is less time consuming. Other reason for choosing this method is the conditions of synthesis in this method are highly controllable and further it provides homogeneous powders of highest yield at temperatures close to 100 °C. Moreover, the influence of Ni-Zn ferrite is reported recently, synthesis and characterization of Ni-Zn ferrites prepared by classical ceramic method and by mechano-synthesis [9, 10] were reported. Ni-Zn-Co ferrites were also prepared and investigated [11]. This paper reports and discusses the results of synthesis and characterization of Ni-Zn-Cu ferrite nanoparticles with respect to the heat treating temperature. In this paper, we report the magnetic properties and Mössbauer spectral studies of a Ni-Zn ferrite synthesized by a co-precipitation method at low temperatures. The

chemically synthesized precursors produce ferrite powders at relatively low temperatures (≤ 600 °C) with greater reactivity and sinterability.

EXPERIMENTAL

Synthesis of the ferrite nanoparticles was done by coprecipitation [12] by taking high-purity $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, FeCl_3 and ZnSO_4 as starting materials. According to the chemical formula of $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, each starting material was weighted separately and added suitable quantity of de-ionized water to make them 0.5M solutions and then mixed all these cationic solutions while stirring to complete dissolution. The NaOH solution is prepared in sufficient quantity at 0.2M concentration and is heated to 60°C. Then, the heated NaOH solution is poured into the cationic solution in a thin flow while maintaining the stirring and heating till the precipitation occurs. Heating of the precipitate in its alkaline condition is continued to a soaking temperature of for 30 minutes in order to complete the reaction. Stirring was maintained further for 6 Hrs for ageing and then the precipitated particles are washed and filtered six times before drying them at 60°C for 48 hours. The co-precipitated ferrite agglomerates were then ground for few minutes using agate mortar and pestle to have very fine particles. These particles were subsequently heat treated at 600, 800, 1000 and 1200°C for further crystallization. The ferrite powder thus obtained (sample A) was divided into six equal parts for calcination at higher temperatures. The calcinations were carried out at four different temperatures from 400 to 1200 °C at an interval of 200 °C and these calcined samples (designated as B-E) were used to study the effect of calcination temperature on the evolution of micro-structurally homogeneous single-phase ferrites and the related magnetic properties. The different samples were characterized by powder X-ray diffraction (XRD) using a Philips PW 1730 diffractometer with Cu-

$\text{K}\alpha$ radiation with Nickel filter ($\lambda = 1.5428$ Å), magnetic measurements, with variable temperatures and applied magnetic fields ($80 \text{ K} \leq T \leq 873 \text{ K}$, $0-15 \text{ kOe}$), using a EG & G PAR model 4500 vibrating sample magnetometer and ^{57}Fe -transmission Mössbauer spectroscopy at variable temperatures and applied magnetic field ($4.2-300 \text{ K}$, 5 T) using a commercial Oxford cryostat. A standard least-square fitting program was used to derive Mössbauer hyperfine interaction parameters.

RESULTS AND DISCUSSION

Ni-Zn ferrite is a soft magnetic ceramic material that has the configuration $(\text{Zn}_x\text{Fe}_{1-x})_A[\text{Ni}_{1-x}\text{Fe}_{1+x}]_B\text{O}_4$, where the subscripts A and B denote tetrahedral (A) and octahedral (B) sites in the AB_2O_4 spinel structure [1]. Every Fe ion occupying an A site is surrounded by 12 nearest neighbours (Ni or Fe ions) at B sites, and every Fe ion at the B site is surrounded by 6 nearest neighbours (Zn or Fe ions) at the A sites. For the hyperfine interaction influencing the Mössbauer spectral lines and their line shapes, we take into our analysis the stronger A-B interactions rather than the A-A or B-B interactions. The different surrounding of a Fe site leads to a varying hyperfine field at each iron nucleus depending on the number of nearest Fe or Ni neighbours (A site) and Fe or Zn neighbours (B site).

The powder XRD patterns of the as-dried powder (A) and the samples calcined at different temperatures (B to E) are shown in Fig. 1. It is evident from the XRD pattern of sample A that a pure single phase spinel is formed, as all the peaks match well with the characteristic reflections of Ni-Zn ferrite. The peaks are broad indicating the fine crystallite nature ($\approx 16 \text{ nm}$) of the ferrite formed. For the calcined samples (B to E) also all the characteristic reflections of Ni-Zn ferrites are seen with increased intensity and sharpness. It implies progressive growth of crystallites and better crystallinity after

calcining at higher temperatures (16–44 nm). This data is also supported by SEM studies on all samples. The M-H curves of the different samples (A-E) are shown in Fig. 2.

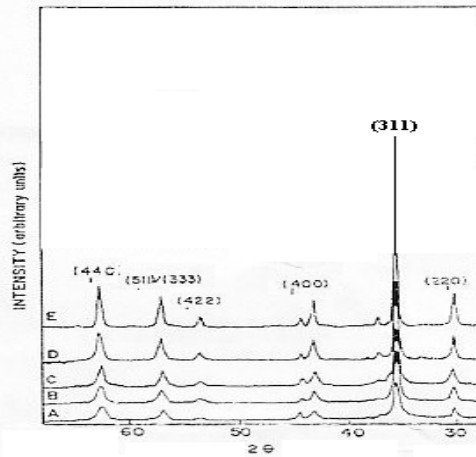


Fig.1- XRD Patterns as-dried samples (A) 400 (B) 600 (C) 800 (D) 1000 (E) 1200

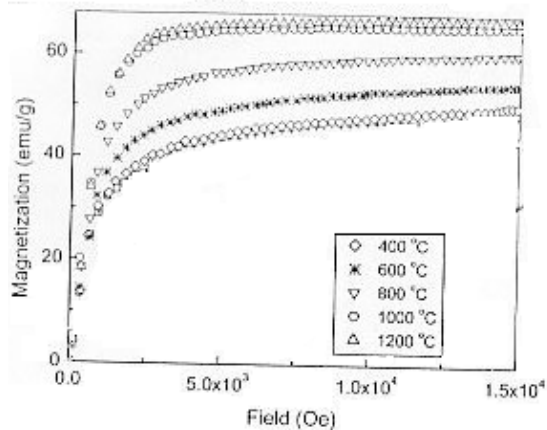


Fig.2- M versus H behavior of as dried samples and those calcined at different temperatures.

The ferrite formed at 80 °C (sample A) shows a continuous increase in the magnetization, and the interesting observation is that the 16 nm crystallites attained the magnetization of 40 emu/g at an applied field of 5 kOe. The other samples have attained much higher magnetization values at 5 kOe fields, confirming the evolution of atomically and microstructurally well-defined ferrimagnetic phase at higher calcination

temperatures. The maximum σ_s value obtained is 96% of the reported value for this composition. Curie temperature (T_c) is obtained as 480 °C, comparable to the literature value for this composition. Figure 3 shows the ^{57}Fe Mössbauer spectra of samples A and G, recorded at 300 and 4.2 K, as well as in the presence of an applied magnetic field of 5 T, at 4.2 K, in the direction parallel to the γ -rays. The Mössbauer spectrum of A at 300 K shows a very broad doublet due to the electron spin relaxation effect attributable to the superparamagnetic nature of the 16 nm ferrite powder. The non-lorentzian nature and the relatively sharp line of the doublet at lower relative velocity indicate a positive EFG parameter. $\Delta E_Q = 0.58$ mm/sec and I.S. = 0.19 mm/sec agree well with the data reported in the literature [3] indicating the presence of Fe^{3+} ions situated in distorted local lattice environments. The random distribution of near neighbours of ferric ions at A and B sites supports the broad nature of the quadrupole doublet. The Mössbauer spectrum at 4.2 K in zero applied field shows a broad sextet pattern indicating the slowing down of the spin relaxation effects of the superfine crystallites. The broad spectrum was fitted with hyperfine field distribution programme and the derived Mössbauer parameters are in agreement with the data reported earlier [3]. The Mössbauer spectrum at 4.2 K in presence of applied magnetic field of 5 T clearly indicates further slowing down of spin relaxation effects resulting in sharp resolved sub-spectra characteristics of Fe^{3+} ions at A and B sites in ferrites [11]. It also shows the effect of H_{app} on inner lines of the sextet ($\Delta m_l = 0$). The Mössbauer spectra for the sample calcined at 1200 °C, shown in Fig. 3, are recorded in the identical way and the derived Mössbauer parameters confirmed the formation of homogenous single phase Ni-Zn ferrite.

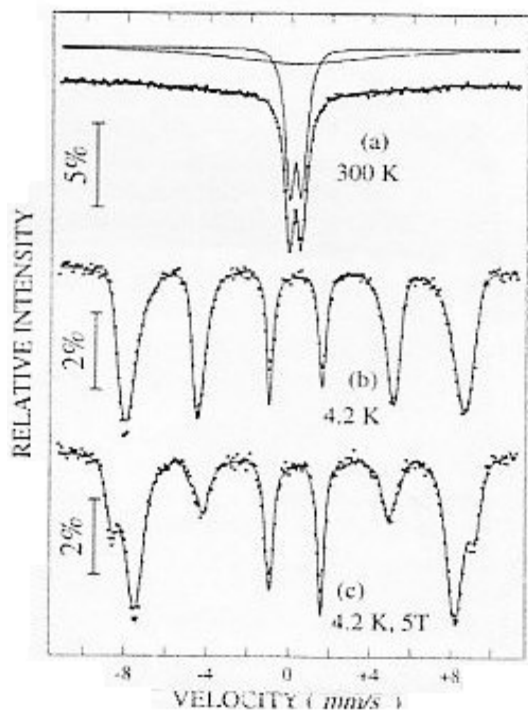


Fig.3- Mössbauer Spectra of sample A

CONCLUSION

In conclusion, powder XRD, VSM and Mössbauer data indicated clearly the formation of ultrafine single phase of Ni-Zn ferrite at low temperatures.

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