Synthesis and characterization of some ferrite nanoparticles

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Three mixed ferrite systems, namely $Ni_{0.65} Zn_{0.375} In_x Ti_{0.025} Fe_{1.95-x} O_4$ (Ni-Zn-In-Ti), $Ni_{0.65} Zn_{0.35} Fe_2 O_4$ (Ni-Zn) and $Mn_{0.75} Zn_{0.18} Fe_{2.07} O_4$ (Mn-Zn) have been chosen for the present study to compare their structural and magnetic characterizations under different ferrite nano preparation routes. Ni-Zn-In-Ti ferrite nanoparticles have been prepared using first by a classical ceramic method to result in sintered ferrite specs and then by mechanosynthesis approach of ball milling to have ultra fine ferrite particles. Ni-Zn and Mn-Zn ferrite nanoparticles were prepared by a soft chemical approach of coprecipitation and then heat treated the particles at different annealing temperatures for improved crystallinity. The samples were then subjected to x-ray diffraction technique, vibrating sample magnetometry and ferromagnetic resonance (FMR) spectrometry and the results are compared and discussed in the light of the existing understanding.

1. Introduction

Ferrites are among the most widely used electromagnetic materials for a broad category of applications over a wide frequency range due to their low cost and high performance [1]. Recently, ferrite research has been shifted towards developing these materials in nanometric scales as the performance in their conventional bulk preparation routes is reaching their limits due to their higher electrical conductivity and domain wall resonance [2,3]. However, the 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 nano scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multi-domain formation, the particle exists in a single domain state and domain wall resonance is avoided; thus the material can work at higher frequencies.

Ferrite particles in nano scales can be produced by a large number of methods. These include soft chemical methods such as coprecipitation of hydroxides [5], sol gel synthesis [6], hydrothermal synthesis [7] and mechano synthesis approach of ball milling [8] etc. It is far from clear whether the different routes produce the same microstructure but the present paper reports the results of the powders of three ferrite systems generated by ball milling and coprecipitation as these routes provide a good control over the particle size and produce samples in relatively short times. In the previous papers [9-11] we reported on the properties of Ni-Zn undoped ferrites and doped by Nb and Ti, prepared by standard ceramic method. The aim of this paper is to report and discuss the results of structural, magnetic and resonance parameters of ball milled Ni-Zn-In-Ti and coprecipitated and heat treated

Mn-Zn and Ni-Zn ferrite nanoparticles in an attempt to throw more light in understanding the physics and chemistry of these new materials at nano scales.

2. Experimental

The ferrite systems of $Ni_{0.65} Zn_{0.375} In_x Ti_{0.025} Fe_{1.95-x} O_4$ (Ni-Zn-In-Ti), $Ni_{0.65}Zn_{0.35}Fe_2O_4$(Ni-Zn) and $Mn_{0.75}Zn_{0.18}Fe_{2.07}O_4$ (Mn-Zn) have been chosen for the present study as these materials are good candidates for power applications beyond 1 MHz. Preparation of nano scaled ferrite particles of these systems was done by two different methods. In the first case, particles were made by ball milling. Sintered pellets of the ferrite system, $Ni_{0.65} Zn_{0.375} In_x Ti_{0.025} Fe_{1.95-x} O_4$, were first made by ceramic method and then they were ground using a Spex 8000 mixer mill. Approximately one gram of pellets were placed in a stainless steel container together with stainless steel balls keeping the ball to powder weight ratio of 10 and the milling was carried out for 5 hours. As milled powders were used for subsequent characterizations. In the second case, synthesis of $Ni_{0.65} Zn_{0.35} Fe_2 O_4$ and $Mn_{0.75} Zn_{0.18} Fe_{2.07} O_4$ ferrite nanoparticles was done by coprecipitation by taking the high purity starting materials as chloride salts for cationic solutions and the sodium hydroxide solution as the base. The heated NaOH solution is poured into the cationic solution in a thin flow while maintaining the stirring at 500 rpm and heating at 100 ^{o}C till the precipitation occurs. The precipitate was washed and filtered repeatedly before drying and this ultimately resulted in very fine particles which were subsequently heat treated at 200, 400, 600 and 800 ^{o}C for crystallization.

The powder samples of all the three systems were then subjected to characterizations. X-ray powder

diffraction patterns of the samples were taken on a Phillips X'pert diffractometer using Cu K_α radiation. Magnetisation measurements were made on a Vibrating Sample Magnetometer at room temperature using a field up to 10 kOe. Room temperature ferromagnetic resonance (FMR) analysis was performed at room temperature using a conventional microwave X-band reflection cavity spectrometer system operated at 9.8 GHz.

3. Results and discussion

Typical XRD patterns of ball milled Ni-Zn-In-Ti ferrite nano particles are shown in Fig. 1. The major peaks indicative of single phase spinel crystal structure were identified in all three systems, but the intensities were observed to be lesser and the peak broadening is higher in the order of coprecipitated Mn-Zn ferrite nanoparticles, ball milled Ni-Zn-In-Ti ferrite samples and coprecipitated Ni-Zn ferrites respectively. The coprecipitated samples are observed to exhibit increased crystallinity with the increase in annealing temperature and growth in crystallite size. However, in case of Mn-Zn ferrites, though the samples exhibit major peaks indicative of spinel crystal structures, they are yet to be fully crystallised.
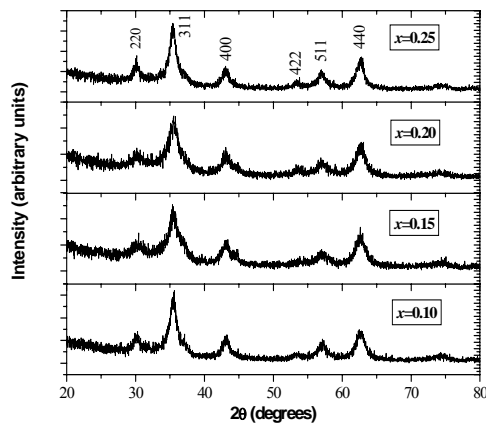

Fig. 1. XRD patterns of ball milled $Ni_{0.65} Zn_{0.375} In_x Ti_{0.025}$ $Fe_{1.95-x} O_4$ ferrite nano particles
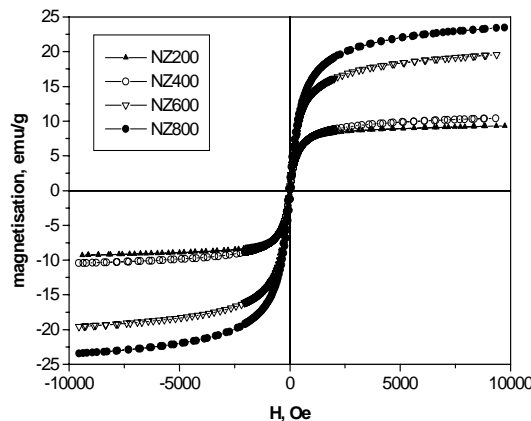

Fig. 2. Hysteresis loops of the coprecipitated $Ni_{0.65} Zn_{0.35} Fe_2 O_4$ ferrite samples.

Average particle size (D) of the ferrites in each case was calculated from the broadening of the respective high intensity 311 peak using the Scherrer equation [12]

$$D = k \lambda / \beta \cos\theta \qquad (1)$$

where k is the Scherrer factor (0.9), λ is the x-ray wavelength, here $\lambda = 1.54178$ Å, β is the line broadening of a peak at angle θ. And β is measured using the following equation [13]

$$\beta = (B^2 - b_o^2)^{½} \qquad (2)$$

where B is the measured FWHM of the experimental profile in degrees and b_o is the instrumental broadening, which was obtained from the scans of standard silicon powder. The calculated sizes of the average ferrite particles for all the samples are listed in Table 1 along with other magnetic parameters.

Since the milling conditions for the ball milled Ni-Zn-In-Ti ferrite particles are the same, all these materials have exhibited similar average particle sizes. Slightly lesser particle size samples in this system are marked with lower peak intensities and increased amorphous nature which may be due to increased surface disorder in milling. In case of coprecipitated samples, the particle sizes are found to increase with increase in annealing temperature in both Mn-Zn and Ni-Zn ferrite systems. However, relatively smaller average particle sizes of Mn-Zn ferrites compared to Ni-Zn ferrites are again for the same reason of more amorphous nature of those samples. Typical room temperature hysteresis loops of the coprecipitated Ni-Zn ferrite samples annealed at different temperatures from 200 to 800 °C are shown in Fig. 2. All the three systems with particle sizes of few nanometer exhibited vanished hysteresis as the particle size decreases and smaller values of magnetisation are observed compared to the magnetisation values of their bulk samples of similar compositions. The observed coercivities, as listed in the table, are very small for all the samples and they have been found to decrease either with the decrease in particle size or with the decrease in annealing temperature.

It is known that the magnetic parameters, particularly magnetisation and coercivity, of nanoferrites prepared by coprecipitation are different from those prepared by ceramic methods due to the inversion degree of distribution of cationic ions between the tetrahedral (A-) and octahedral sites (B-) of the spinel lattice [14] and also due to the spin disorder in the shell around the core [15]. It implies that the cations in nanoscale materials occupy lattice sites by a certain degree against their preferences in bulk materials and this degree (of inversion) is dependent on particle size. Since the magnetic parameters, within the same composition under investigation, are determined by microstructural features such as particle size and size distribution, there have been reports of changing the particle size and thereby the inversion degree and magnetic properties by an appropriate heat treatment [16].

In the present study of coprecipitated Ni-Zn and Mn-Zn ferrite systems, the increase in magnetisation with the increase in annealing temperature could be understood as a result of the increase in particle size and thereby the change in degree of inversion parameter, i.e., there are more Ni^{2+} ions occupying A-sites and also more Zn^{2+} ions occupying B-sites in smaller Ni-Zn ferrites resulting in lower magnetisations for those samples. The observed lower values of coercivity with the decrease in annealing temperature and particle size can be explained as due to the localised randomizing effects of thermal energy of a disordered shell of a particle compensating the magnetic contributions made by its core. As the particle size further decreases, this may well lead to zero coercivities and a transition from ferrimagnetic to superparamagnetic state. The deduced magnetic parameters from the hysteresis loops of coprecipitated particles are in accordance with the above.

In the case of Ni-Zn-In-Ti ferrites, the balls continuously collide with sintered ferrite specs during milling leading to material modification by pushing the atoms from their normal positions and splitting the molecules into pieces. In the process, the ferrite system tends to loose its degree of crystallinity which in turn generates defects and partial amorphization resulting in a decrease in the average particle size. This contributes to degrade the intrinsic magnetic parameters [17] as evidenced in the magnetisation values of these samples listed in Table 1. Interestingly, as the average particle size and magnetizations decrease, it is expected that the area of the hysteresis loops vanish and the particles exhibit a behaviour leading to superparamagnetic state after prolonged milling. The observed magnetic parameters from the hysteresis loops of Ni-Zn-In-Ti ferrites are in agreement with their respective particle sizes and the arguments made above.

Typical ferromagnetic resonance (FMR) spectra for Mn-Zn ferrite nanoparticles annealed at different temperatures from 200 to 800 $^{\circ}$C are shown in Fig. 3. The data on the resonance fields were used to estimate magnetic parameters from the spectra and they are listed in Table 1 along with other parameters.

All the samples of three systems under investigation showed single resonance peaks, but each of them is slightly asymmetric. This asymmetric nature is more for the samples of same composition (of coprecipitated Ni-Zn and Mn-Zn ferrites) but subjected to different heat treatments than for those of different compositions of ball milled Ni-Zn-In-Ti ferrites. The asymmetric nature, in general, could be due to the contribution of non uniform resonance modes apart from the main mode of resonance. In respect of coprecipitated samples of the present study, since the compositions under investigation are the same and only the heat treatment is different, the gyromagnetic ratio is supposed to be the same for all the samples and then the particle size and the resulting magnetisation obviously would be expected to influence the FMR parameters [18].

Whereas for Ni-Zn-In-Ti samples, since the particle sizes of all the samples remain similar, the influence shown by these particles on the asymmetry is also expected to be the same for all the samples and, therefore, the intrinsic properties due to compositional variations such as, magnetisation and reduction of the quantity of Fe^{3+} ions on each step, are attributed to the line broadening and asymmetry in different samples. The observed values of resonance field and line width, as listed in the table, are also in accordance with the above.
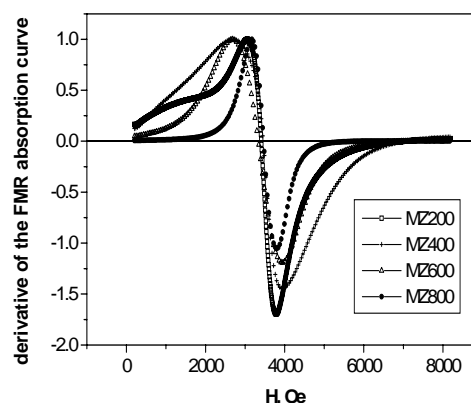

Fig. 3. FMR spectra for $Mn_{0.75}Zn_{0.18}Fe_{2.07}O_4$ ferrite nanoparticles.

4. Conclusions

In conclusion, the X-ray diffraction patterns of all the samples confirm single phase cubic spinel structure. Coprecipitated Ni-Zn ferrites displayed better degree of crystallinity than the Mn-Zn ferrites which are slightly amorphous in nature. The ball milled Ni-Zn-In-Ti ferrite samples experience smaller intensities and higher line broadening due to surface disorder introduced during milling. The average particle sizes of the samples deduced from the 311 XRD peak broadening have been observed to lie in the range from 2-16 nm. The samples were resulting in smaller magnetisations and coercivities as the annealing temperature is lowered and this was attributed to particle size and inversion parameter.

The FMR spectra and the deduced parameters such as resonance field and line width are in accordance with the particle size and magnetisation data of different systems. Further measurements are underway to complement the particle size as well as superparamagnetic nature which could help to understand the system more clearly.

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