

Cation distribution of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles

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Abstract

A set of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples were prepared by citrate precursor route to investigate the growth mechanism and its effect on cationic distribution. Following the information from DTA–TGA analysis, samples were annealed at 550 °C, 700 °C and 750 °C. Magnetization and Mössbauer studies suggest that initially the cationic distribution deviates from its normal preferences but it gets back to the normal preference at a temperature around 675 °C. It has been found that size onset for having the bulk cation configuration exclusively depends on the composition.

Keywords: Mössbauer Spectroscopy; Ferrite; Nanoparticles, Cationic distribution

1. Introduction

Ferrites are technologically important material and an object of study for quite long time (Ishino *et al.*, 1987; Smit *et al.*, 1959). Nickel-Zinc ferrite has been extensively used as high permeability material. Research in this field has received a major boost in the recent years when new techniques for synthesis and characterization of nanoparticles in the range 5-20 nm were developed. Several research groups are exploring the possibility of preparing ferrites with novel properties by forcing the system to acquire metastable and non-equilibrium configurations (Albuquerque *et al.*, 2000; Vanderzalgetal *et al.*, 1996; Fanin *et al.*, 1999; Bercoff *et al.*, 2000). Apart from the application aspects, investigations have been directed towards understanding the basic physics of nanophase interactions. Synthesizing these materials in nanophase leads to different exotic properties (Hamdeh *et al.*, 1997; Goya *et al.*, 1993; Upadhyay *et al.*, 2001; Rath *et al.*, 2000). The magnetic properties of these ferrites are mainly controlled by the cation distribution of Ni, Zn and Fe among the available tetrahedral A sites and octahedral B sites (Smit *et al.*, 1959). Zinc is known to have a high degree of affinity for the tetrahedral sites in the spinel structure and nickel has a similar affinity for octahedral B site. Hence bulk nickel ferrite is a model 'inverse' ferrite while bulk zinc ferrite is a model 'normal' ferrite. The sample having both the cations is termed as "mixed" ferrite (Navrotsky *et al.*, 1968).

The cation preferences can be greatly altered by preparing the spinel ferrites in nanosize. Several reports have indicated that for particle size less than or around 10 nm, sizeable fraction of zinc present in spinel structure occupies octahedral B sites, against its normal preference. The magnetic properties are likewise altered once the cation distribution is changed (Ma *et al.*, 2000; Albuquerque *et al.*, 2001; Uen *et al.*, 1982). $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ offers the most complex cationic distribution in the series of Ni-Zn ferrites. Most of the studies on nanophase ferrites therefore have been associated with the cationic distribution in the structure. However, very less emphasis has been paid on the growth process of these systems. In this investigation we have attempted to study the systematic growth of this system by allowing the particles to grow under the influence of thermal energy and study their magnetic and cationic distribution in the structure by vibrating sample magnetometer and Mössbauer spectroscopy.

2. Materials and Methods

A large number of researchers have used citrate precursor method for the synthesis of ferrites in bulk as well as in nanosize (Sato *et al.*, 1990; Ueda *et al.*, 1993; Guaita *et al.*, 1999; Vijyalakshmi *et al.*, 1998; Kamble R.C *et al.*, 2010; Verma *et al.*, 2006; Sankara

Narayanan et al., 1994; Choy et al., 1994, Costa et al., 2003; Gajbhiye et al., 1996, Seema et al., 1998; Verma et al., 1999). In this method citrates/acetates of the salts are homogenized in presence of citric acid, and proper refluxing, drying and further annealing leads to the final product. For instance, Verma et al. (1999) used nickel nitrate, zinc nitrate, iron(III) citrate and citric acid to prepare Ni-Zn ferrite. In their work, the homogenized nitrate/citrate solution was heated at 40 °C for about 30 min and added to ferric citrate solution under constant stirring. The dried citrate mixture was calcined for 1/2 hour at 1000 °C to obtain the spinel ferrite. Guatia et al. (1999) extensively studied the role of precursor on the formation of zinc ferrite. The purity, stability and uniformity in particle size depended crucially on the process parameters such as concentration of salt solutions, refluxing time, cooling rate and so on. In the present study the citrate route was followed for synthesis of nickel-zinc ferrite.

The starting materials used for preparation of nickel-zinc ferrite were: ferric citrate, zinc acetate, nickel nitrate and citric acid. Ferric citrate, nickel acetate and zinc acetate were taken in stoichiometric proportion and their aqueous solutions were prepared separately (concentration 0.5 mol/L each) by dissolving them in distilled water under constant stirring to facilitate dissolution. The solutions were then mixed together. Citric acid solution (concentration 0.5 mol/L) was prepared separately and added to the aqueous salt solution with salt solution to citric acid ratio 1:4. The solution was then heated to 80 °C and maintained at that temperature for 2 hours in a round bottom flask using a heating mantle under constant refluxing and stirring conditions using a magnetic stirrer. The refluxed solution was then slowly cooled to form a viscous solution. Finally, the viscous solution was dried at 60 °C for 24 hours to form a brown fluffy mass, which was crumbled to form the precursor powder. In order to determine the temperature range for growth of these systems Differential Thermal Analysis and Thermo Gravimetric Analysis in temperature range 40°C -700°C was performed. Figure 1 shows the DTA-TGA plot.

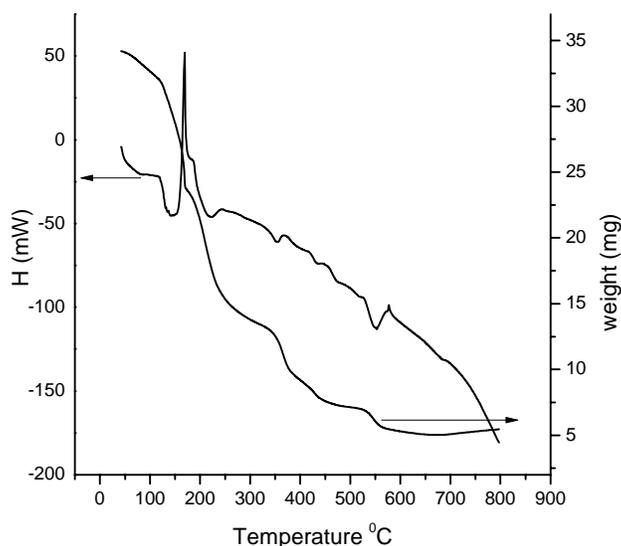


Figure 1. DTA-TGA plot of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$.

It may be noted that the transformation from precursor powder to final phase is accompanied in several steps. The very first weight loss around 120°C can be attributed to vaporization of water molecules from surface and then at 200 °C from the trapped water. In order to decompose the citrate network, higher temperature is needed and that is evident from the weight loss at 350 °C. The conversion process starts at around 410 °C and finally get converged into the well grown ferrite particles at a temperature 550 °C. The thermogravimetric analysis goes in sync with the DTA curve as well where we see a significant endothermic peak. This gives an indication that the ferrite formation get completed at a temperature around 550 °C. However after further increase in the temperature another peak is seen in the DTA curve at 700 °C and the slight increase in the weight of the sample which continues to grow. Considering these facts we annealed the precursor powder at 550 °C, 700 °C and 750 °C for 1 hour so that a better insight about the mechanisms of the growth can be obtained.

4. Results and Discussion

Figure 2 shows the X-ray diffraction of the samples annealed at different temperatures. All the peaks could be indexed with spinel ferrite structure showing that all the samples were formed in single phase and were well crystalline in nature. The particles size of these samples has been calculated using Williamson-Hall method. The average particle size of the sample annealed at 550 °C turns out to be around 45 nm. On further increase in the annealing temperature to 700 °C, the size increased to 51 nm.

However as expected there is very little change in the particle size of the sample annealed at 750 °C. This is consistent with the DTA-TGA analysis.

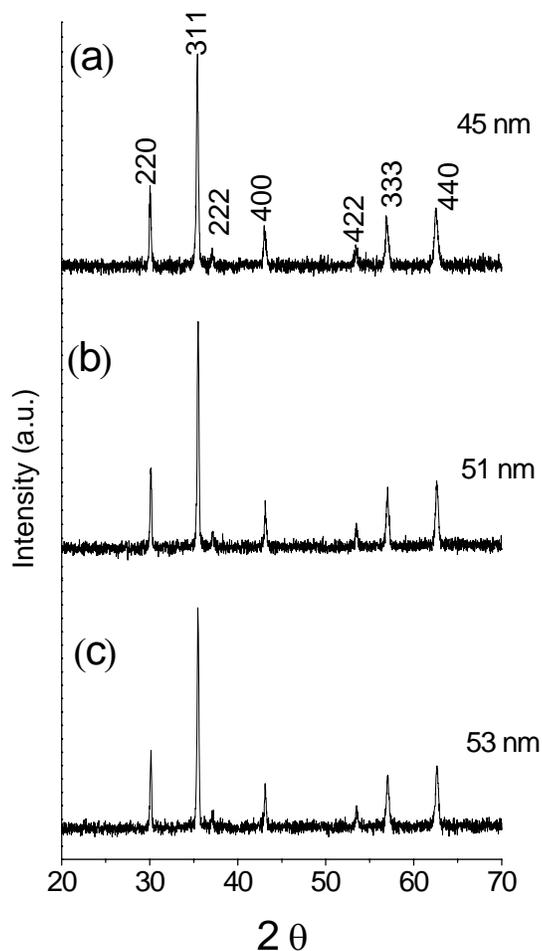


Figure 2. X-ray diffraction pattern of samples annealed at (a) 550 °C (b) 700 °C and (c) 750 °C

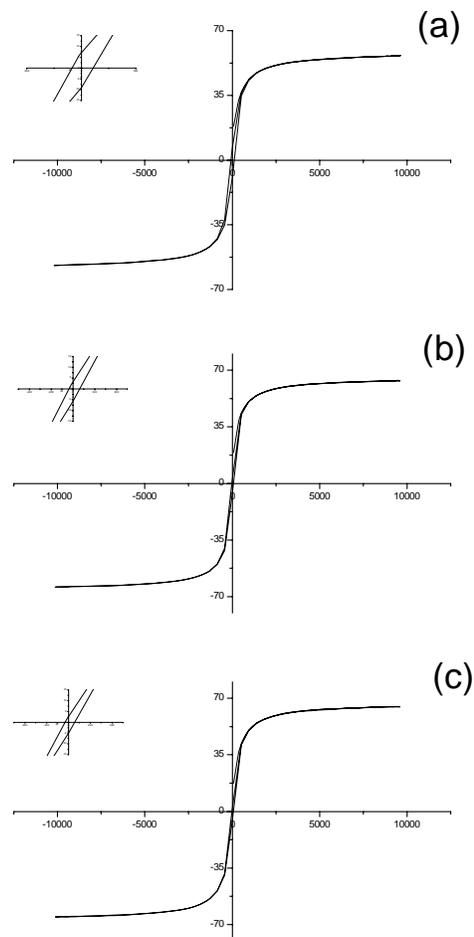


Figure 3. M vs H loop of the samples annealed at (a) 550 °C (b) 700 °C and (c) 750 °C

In order to look into the magnetic behaviour of these samples magnetization studies were carried out. Figure 3 shows the M vs H loop of these samples. The inset of each graph shows the behaviour of the sample at low applied field. Here also we see striking difference between the samples annealed at 550 °C and 700 °C. The sample annealed at 550 °C shows a saturation magnetization value of 56.0 emu/g, whereas the sample annealed at 700 °C shows that of 64.4 emu/g. This clearly indicates that the magnetic configurations of these samples are different. It may be noted here the DTA curve (Figure 1) shows an endothermic kink at a temperature around 675 °C. It is now attempted to explain the low value of saturation magnetization of the sample annealed at 550 °C, in comparison with the sample annealed at 700 °C.

It is known that the cations in Ni-Zn ferrite have a very strong preference for a particular site when these are in bulk form. Mainly it is octahedral preference for Ni and tetrahedral preference for Zn. Considering these preferences and composition, the bulk configuration can be written as $(\text{Zn}_{0.5}\text{Fe}_{0.5})[\text{Ni}_{0.5}\text{Fe}_{1.5}]\text{O}_4$. Such a configuration leads to the saturation magnetization value of nearly 70 emu/g at room temperature (Naughton *et al.*, 2007). However in case of nanoparticles of these systems, the cation preferences does not hold good any more. That means some of the Zn will now occupy the octahedral sites and push back Ni and Fe to the tetrahedral sites (Hamdeh *et al.*, 1997; Goya *et al.*, 1999; Rath *et al.*, 2000; Upadhyay *et al.*, 2001). This new configuration can now be written as $(\text{Zn}_{0.5-x}\text{Fe}_{0.5-y}\text{Ni}_z)[\text{Ni}_{0.5-z}\text{Zn}_x\text{Fe}_{1.5-y}]\text{O}_4$ such that $(x=y+z)$. Such a substitution definitely leads to the lower value of the saturation magnetization which is indeed the case in our system, where the saturation magnetization value is 56.01 emu/g.

Having a relatively low value of saturation magnetization for the sample annealed at 550 °C indicates that cations are surely deviated from their normal preferences. When annealed at higher temperature, the cations under the influence of the heat energy tries to regain their normal preferences, which leads to the higher value of the saturation magnetization in the samples annealed at 700 °C and 750 °C. It seems that a temperature of 675 °C is sufficient enough to trigger the cationic redistribution which is further reflected in DTA curve as an endothermic kink. Beyond this temperature we don't see any changes neither in magnetization value nor in DTA or particle size. All these measurements clearly indicate that a temperature of 675 °C is sufficient to achieve the bulk cation preferences in the spinel structure.

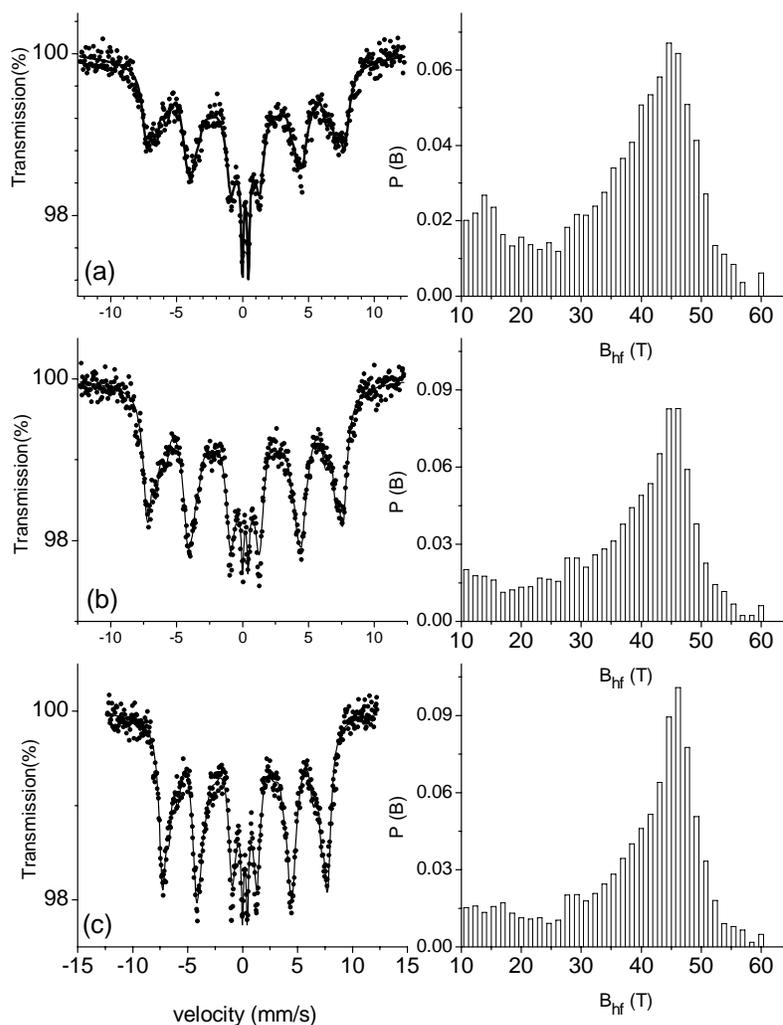


Figure 4. Mössbauer spectrum and the probability distribution of HMF of the samples annealed at (a) 550 °C (b) 700 °C and (c) 750 °C.

In order to have a more conclusive proof of redistributed cations we performed Mössbauer spectroscopy of these samples. Figure 4 shows the room temperature Mössbauer data of different samples. The $p-H$ distribution has been calculated using the Window's approach (Window, 1971). The spectra of all the samples have both magnetic and quadrupole components. The doublet in the spectrum may have its origin from the fact that the smaller nanoparticles of Ni-Zn ferrites in the sample may exist in superparamagnetic phase. The relatively bigger particle in the distribution may also contribute by collective magnetic excitations. This is evident in the Mössbauer spectrum where we don't see uniquely defined sets of HMF (hyperfine magnetic field).

The very first striking difference is seen in reduction of doublet area as the sample gets annealed from 550 °C to 700 °C and a strong emergence of magnetic component. A supply of heat energy facilitates the grain growth and thus the cations to redistribute back to their bulk preferences.

Our hypothesis that some of zinc occupies octahedral sites deduced from magnetization data get further supported by the Mössbauer spectroscopy. The presence of zinc at octahedral site will weaken the magnetic ordering in the spinel structure which

will lead to the emergence of a non magnetic doublet. Furthermore, when comparing with the magnetic component, the value of hyperfine magnetic field of the most dominant component gets enhanced from 440 kOe to 460 kOe. This indicates that the cations have acquired their normal preferences after getting annealed 700 °C. However we see no further change in either the saturation magnetization value or in the value of HMF of the magnetic component after annealing the sample at 750 °C apart from the distribution getting narrower, which is an indication that the cationic distribution is just getting refined to its bulk structure.

Meanwhile, in our earlier studies we had noticed that in case of nanosized Zn ferrite, a particle size of 14 nm was sufficient enough to bring out the normal cation distribution in the structure i.e. there is no deviation from the normal preference of zinc occupying the tetrahedral site (Upadhyay *et al.*, 2007). However in the case of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ a particle size of even 45 nm is holding the deviated preference of the cations. It seems that the onset particle size for having the bulk configuration depends crucially on the composition of the system although having the similar crystallographic structure. This hypothesis can be a matter of further investigation.

5. Conclusions

1. With a view to look into the growth mechanism and its effect on cationic distribution a set of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples were prepared by citrate precursor route. DTA–TGA analysis suggested that the growth of the sample is almost complete at 550 °C, therefore the set of samples were prepared by annealing the citrate precursor at 550 °C, 700 °C and 750 °C.
2. Magnetization and Mössbauer studies suggest that initially the cationic distribution is deviated from the normal preferences in the structure, which gets back to its normal preference at a temperature around 700 °C. When compared with the results of our previous studies, it has been found that the onset particle size for having the bulk cation configuration crucially depends on the composition of the system. While a size of 14 nm was sufficient enough to bring back the bulk cationic configuration for ZnFe_2O_4 , for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, even 45 nm was not sufficient enough for the same. The very first striking difference is seen in reduction of doublet area in Mossbauer spectrum as the sample gets annealed from 550 °C to 700 °C and a strong emergence of magnetic component. A supply of heat energy facilitated the grain growth and thus the cations redistributed to their bulk preferences

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