Structural, dielectric and magnetic properties of superparamagnetic zinc ferrite nanoparticles synthesized through coprecipitation technique

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Abstract

Nanosized spinel zinc ferrite was reproducibly synthesized via coprecipitation technique, and effects of variation in digestion temperature on the structural, dielectric and magnetic properties were studied. The crystallite size was found in the range of 4.4–15 nm. X-ray diffracion results revealed that the synthesized materials were of pure normal spinel structure. A very small value of coercivity was observed corresponding to the superparamagnetic behavior of the samples. The dielectric constant measured at 300 K in the frequency range of 600 Hz to 1 MHz showed an exponential decay with increasing frequency. It was observed that the particle size increased with an increase in digestion temperature while saturation magnetization (Ms) decreased. These particles are suitable to be used as Magnetic Resonance Imaging contrast agent.

Key words: spinel structures, zinc ferrites, coprecipitation, superparamagnetism, dielectric constant

1. Introduction

Recently, ferrite nanoparticles (NPs) have attracted great attention due to the controllability of superparamagnetic and magnetic single domain behavior [1]. The current interest has been to make nanosized ferrite particles to reduce energy losses associated to bulk powders. ZnFe2O4 is an important member of spinel structured ferrite family [1]. The synthesis of nanocrystalline spinel Zn ferrite has been investigated extensively in recent years due to its physical [3], chemical [3] and magnetic [4–6] properties. They have potential applications in electronic and telecommunication industries [3] like magnetic core [1, 7], high-density magnetic recording [6], photoelectrochemical cells [2, 7], photoinduced transformer [2, 7], magnetic fluids [2, 7, 8], high frequency usage [9, 10], gas sensors [11], absorbent material [10] and MRI contrast agent.

When the particle size reduces to nanometer scale some new amazing mechanisms emerge such as superparamagnetism, quantum magnetic tunneling, spin canting, etc. [6, 11–13]. The magnetic properties of nanoferites depend on the particle size and the preparation route that result in superparamagnetism at room temperature [6, 9, 11–13]. The synthesis route plays a pivotal role because samples prepared by different processes show different magnetic properties [14]. Due to small size, ZnFe2O4 NPs exhibit interesting magnetic properties which are significantly different from those of the bulk, such as inversion parameter, magnetization, superparamagnetic relaxation behavior, surface effects that may lead to spin-canting structure [6]. The magnetic properties of spinel-phase oxides are rich and complex [2, 4, 15–17]. Different magnetic ordering exists in Zn ferrites due to various kinds of superexchange interactions between tetrahedral and octahedral site cations [13, 17]. Zn ferrites ex-
hibit magnetization of different orders of magnitude even if having the similar size of particles due to the inversion of Zn and Fe ions over tetrahedral and octahedral sites [9]. Some reporters have shown the coexistence of antiferromagnetism and ferromagnetism in nanosized Zn ferrites while others showed the formation of superparamagnetic domains in nanosized Zn ferrites at room temperature [9].

Spinel structure is made up of a close-packed fcc array of oxygen atoms in which tetrahedral and octahedral interstitial sites are occupied by cations [2, 13, 18]. ZnFe$_2$O$_4$ contains two different cationic sites such as 8 tetrahedral sites and 16 octahedral sites while zinc ions occupying the tetrahedral sites and all the ferric ions occupy the octahedral site [2, 12, 18–20]. ZnFe$_2$O$_4$ is paramagnetic at room temperature having Neel temperature of 10 K [2, 9, 18, 20]. Redistribution of cations in zinc ferrite results when the particle size approaches nanoregime [9, 11, 13]. The transformation from normal to the mixed spinel structure affects the properties of Zn ferrites particularly during the reduction of particle size [9]. Neel temperature, degree of inversion and interaction between octahedral and tetrahedral sublattices of zinc ferrite depend upon particle size [5, 21]. In special synthesis condition, some Fe$^{3+}$ ions may occupy tetrahedral, as well as octahedral sites forming the inverse spinel structure. There are three types of superexchange interactions in spinel ferrites which are due to interaction between the two metal cations keeping oxygen in the middle. These interactions are namely A-O-A, B-O-B, A-O-B [2, 18]. Pure bulk ZnFe$_2$O$_4$ has only B-O-B interaction because Zn$^{2+}$ sitting at an A site does not have magnetic moment [14, 21]. The Neel temperature of the spinel ferrite depends on the strength of all the three superexchange interactions. In spinel ferrites A-O-B interaction is the strongest and A-O-A interaction is the weakest [14, 18]. Cation inversion, i.e., shifting of Zn ions changes the magnetic behavior of the system and the structure of zinc ferrites [8, 9, 18]. In contrast, the nanosize ZnFe$_2$O$_4$ with the mixed spinel structure has a much higher ferromagnetic ordering temperature that in some cases can reach the value as high as 450 K [2, 21, 22].

Magnetic properties, such as the saturation magnetization, remanence magnetization and coercivity, primarily depend on the method of preparation of Zn ferrites [24, 25]. In recent years, ZnFe$_2$O$_4$ NPs prepared using varied methods, such as liquid phase chemical [7], hydrolysis in polyl medium [12], nitrate method [9], ultrasonic emulsion and evaporation [11], chemical coprecipitation [8, 17, 20, 26], coprecipitation citric acid method [3], traditional ceramic synthesis [27], facile self-propagation combustion [21], aerogel procedure [1, 13, 20, 28], pulsed wire discharge (PWD) [10, 29], low-temperature hydroxide coprecipitation and hydrothermal synthesis [16], high energy ball milling [15, 18, 25, 30], electrodeposition technique [25], hydrothermal reaction [14] have been extensively studied. Of all these techniques, chemical coprecipitation seems to be the most convenient for the synthesis of NPs because of its simplicity and better control over crystallite size and other properties of the materials. Current research efforts are being directed to synthesize superparamagnetic Zn ferrites by coprecipitation technique and to make detail studies of effect of digestion temperature on their magnetic and dielectric behavior.

2. Experimental procedure

The chemical coprecipitation method was adopted to synthesize superparamagnetic Zn-ferrite. The metal ion solution was prepared by adding chlorides of zinc and ferric into distilled and deionized water. A 1 molar solution of NaOH was prepared separately in deionized water. The solution containing the metal ions was mixed drop wise into the NaOH solution with rigorous mechanical stirring on a magnetic stirrer. The solution thus formed kept under isothermal static conditions in a preheated water bath for digestion treatment. Each sample was treated from 40°C to 95°C in steps of 20°C for constant time interval of 150 min. The precipitates were filtered and washed with deionized water and dried in an oven at 60°C. The powders were pressed into pellets 8,000 psi pressure.

Zinc ferrite samples were characterized for structural and compositional properties at room temperature using PANalytical X-ray diffractometer system with Cu Kα (λ = 1.5406 Å) in 2θ range of 10 to 70 degree. Surface morphology was observed by scanning electron microscopy (SEM, Hitachi S-4700) which gave ultra fine uniform distribution of particles (Fig. 1). Magnetic properties were examined by Lake Shore 735 Vibrating Sample Magnetometer (VSM). Small
The particle size $D$, lattice constant $a$, X-ray density $\rho_x$, measured bulk density $\rho_m$, specific surface area $S$, porosity $P$ of samples

| Sample | $T$ (°C) | $D$ (nm) | $a$ (Å) | $\rho_m$ (g cm$^{-3}$) | $\rho_x$ (g cm$^{-3}$) | $P$ | $S$ |
|--------|---------|---------|---------|--------------------------|------------------------|-----|-----|
| T1     | 55      | 4.4     | 8.463   | 2.54                     | 5.44                   | 0.5331 | 250.67 |
| T3     | 75      | 6.6     | 8.457   | 3.26                     | 5.399                  | 0.60382 | 168.38 |
| T5     | 95      | 15      | 8.416   | 2.48                     | 5.445                  | 0.54454 | 73.462 |

The temperature $T$, particle size $D$, coercivity $C$, retentivity $R$ and saturation magnetization $M_s$, magnetic moment $M_m$ and concentration of charge carriers $n_c$

| Sample | $T$ (°C) | $D$ (nm) | $C$ (Gauss) | $R$ (emu g$^{-1}$) | $M_s$ (emu g$^{-1}$) | $M_m$ (Bohr magnetons) | $n_c$ |
|--------|---------|---------|------------|-------------------|---------------------|-----------------------|-------|
| T1     | 55      | 4.4     | 131.18     | 16.29E-3          | 0.47266             | 0.0803                | 1.2684 × 10$^{22}$ |
| T3     | 75      | 6.6     | 26.93      | 3.16E-3           | 0.451873            | 0.00687               | 1.6280 × 10$^{22}$ |
| T5     | 95      | 15      | 8.463      | 2.54              | 0.439               | 0.00764               | 1.2385 × 10$^{22}$ |

volume of the prepared compositions was applied on the sample holder in the magnetic field of the coils for VSM to calculate the magnetic properties. For the measurement of dielectric constant of the samples, silver paint was applied on the flat surfaces of the pellets and air-dried to have good ohmic contacts. The capacitance of the samples was measured using a WAYNE KERR 4275 LCR Meter Bridge at room temperature and then the dielectric constant was calculated with changing frequency in the range from 60 Hz to 0.1 MHz.

3. Results

The structure and crystallite size of prepared zinc ferrite samples were determined by XRD analysis. All the observed peaks correspond to standard spinel diffraction patterns with no extra peak, which confirmed the single phase cubic structure. The XRD pattern showed that the strongest reflection came from the (311) plane for all the samples. The particle size, measured bulk density, specific surface area, porosity and X-ray density were calculated by Eqs. (1), (2), (3) and (4), respectively:

$$D = 0.89\lambda / \beta \cos \theta,$$

$$\rho_m = 8M / N a^3,$$

$$S = 6000 / \rho_x D,$$

$$P = 1 - (\rho_m / \rho_x).$$

Equation (1) represents the Sherrer’s formula, in which $D$ is the crystallite size in nm, $\lambda$ is the wavelength of Cu Kα (0.15406 nm), $\theta$ is the corresponding diffraction angle, 0.89 is the Sherrer’s constant, and $\beta = B - b$, where $B$ is the full width at half maximum of the peak in radian, $b$ is the instrumental line broadening. Particle sizes were cross confirmed by scanning electron microscope. In Eq. (2), $M$ is the molecular weight of the samples, $N$ is the Avogadro’s number, $a$ is the lattice parameter. In Eq. (3), $D$ is the crystallite size in nm and $\rho_x$ is the X-ray density in g cm$^{-3}$. In Eq. (4), $\rho_m$ is the measured bulk density and $\rho_x$ is the X-ray density. Table 1 shows the particle size, lattice constant, X-ray density, measured bulk density, specific surface area and porosity.

Magnetic properties were examined by VSM as shown in Figs. 2a, b, c, which showed very small remanent magnetization of ferrite particles. The $B$-$H$ curves at room temperature showed the ideal soft ferrites with extremely narrow loops and very low hysteresis losses. Under optimal conditions, a very small inversion has been observed in the samples leading to superparamagnetic behavior. The shape of VSM line showed the considerable magnetic ordering at room temperature [18]. The sample shows a saturation magnetization of about 0.439 emu g$^{-1}$ at room temperature.

Magnetic moment and concentration of charge carriers were calculated by Eqs. (5) and (6), respectively:

$$n = (M_s X MoI W_t) / (5586 \rho_m),$$

$$n = (N \rho_m P_{fe}) / M.$$

In Eq. (5), $n$ is the magnetic moment of the samples expressed in Bohr magnetons, $M_s$ is the saturation magnetization and $\rho_m$ is the measured bulk density. In Eq. (6), $N$ is the Avogadro’s number, $M$ is the molecular weight of the compound, $P_{fe}$ is the number of iron atoms in the chemical formula of the ferrites, $\rho_m$ is the measured bulk density. Table 2 shows the temperature, particle size, coercivity, retentivity and
saturation magnetization, magnetic moment and concentration of charge carriers.

The capacitance and dielectric constant of all the samples were measured in the frequency range of 60 Hz to 1 MHz using Eq. (7):

$$\varepsilon' = \frac{C d}{A \varepsilon_0}. \quad (7)$$

In this equation, $C$ is the capacitance of the pellet in F, $d$ is the thickness of the pellet in m, $A$ is the cross-sectional area of the flat surface of the pellet and $\varepsilon_0$ is the permittivity constant of the free space.

4. Discussion

Dielectric constant was measured in the range of 600 Hz to 1 MHz, which exponentially decreased with increasing frequency and this variation in dielectric constant is due to the space charge polarization. This result is in agreement with the results published by Ghatak [13, 33]. In the frequency range, the dielectric constant initially decreased with frequency, then reached a constant value at higher frequency range [34] as shown in Fig. 3. The value of dielectric constant was much higher at lower frequencies and it decreased with the increase in frequency [35–37]. At very high frequencies, its value became so small that it became independent of frequency. The variation in dielectric constant might be due to the space charge polarization which was produced due to the presence of higher conductivity phases in the insulating-matrix boundaries of dielectric [35–37]. Localized accumulation of charges affected the electric field. Polarization decreased with increase of frequency, reaching a constant value at high frequency, beyond which the dipoles could not follow rapid variation of alternating electric fields. The assembly of space charge carriers in a dielectric took a time to line up their axes parallel to an alternating electric field. If the frequency of the field reversal increased, a point was reached where the space charge carriers could not keep up with the field and the alternation of their direction lagged behind that of the field [13, 31–37].

The equilibrium distribution of cations in the spinel structure depends on ionic radii, electronic configurations, electrostatic energies and polarization effects [2, 9, 15, 18, 20]. It was observed that the distribution of cations in octahedral and tetrahedral sites changed as the crystallite size decreased and that this
The particle size increased from 4.4 nm to 15 nm with increasing the digestion temperature from 55°C, 75°C and 95°C, which is well in agreement with the previously reported work by Singh [9], Chinnasamy [30]. The particle size increased with the increase of digestion temperature while the coercivity decreased. This result is in good agreement with the results published by Li [3] and Mozaffari [38]. Surface morphology was investigated by SEM which indicated that the zinc ferrite has a narrow ultra fine uniform particles shape and size distribution of the surface is almost free from defects. Hysteresis loop with zero coercivity shows that the nanocrystalline zinc ferrites have superparamagnetic behavior. This result is in agreement with a previously published work of Chinnasamy [30] and Kumar [39]. A direct correlation was found between particle size and saturation magnetization, that finer the particles, more the saturation magnetization [6, 16, 40]. The variation of saturated magnetization can be explained on the basis of systematic cation distribution and super-exchange interaction [41]. Small antiferromagnetic particles can exhibit superparamagnetism and weak ferromagnetism due to uncompensated spins in the two sublattices [29]. The magnetic properties in nanostructured zinc ferrite system are believed to arise due to the formation of superparamagnetic domains, coexistence of ferrimagnetic and antiferromagnetism [12]. Crystallographically the sample has a single phase [18]. At 300 K, the absence of hysteresis, immeasurable remanence, coercivity, and the non-attainment of saturation indicate the presence of superparamagnetic behavior [10]. The magnetization is found to increase as the particle size decreases and its large value is attributed to the cation inversion associated with particle size reduction [30]. The occurrence of tetrahedral sites by zinc atom increased with the decreasing particle size [31].

5. Conclusions

The crystallite size was controlled to a certain degree by the coprecipitation synthesis technique. The synthesized NPs exhibit the pure cubic spinel phase. VSM results showed the existence of typical superparamagnetic nature of the ZnFe$_2$O$_4$ NPs at 300 K having an average particle size ranging from 4 nm to 15 nm. The magnetic properties correspond to nearly ideal soft ferrites. Saturation magnetization increased with decreasing the particle size which further strongly depended upon digestion temperature and preparation technique. The magnetic properties of nanoferrites depend on the particle size and the preparation route. Particle size increased by increasing the digestion temperature, and saturation magnetization increased as the particle size and digestion temperature decreased.

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