Infrared and magnetic study of nanophase zinc ferrite

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Nanophase zinc ferrite (ZnFe$_2$O$_4$) has been prepared by co-precipitation under stoichiometric conditions. The effect of reactant concentration on particle size has been studied using XRD, structural details using IR absorption spectroscopy, thermal properties using TG/DTA analysis and magnetic moment using SQUID magnetometer measurement. IR spectroscopy has been found to be an important tool for characterizing nanophase ZnFe$_2$O$_4$ particles size in the range 4 – 28 nm. The positions of the absorption band are found to be particle size dependent. The large increase in magnetization with decrease in particle size may be due to super exchange interaction between Fe$^{3+}$ ions on two sublattices A and B. The morphology of the sample has been investigated by TEM and selected area electron diffraction pattern.

\textbf{Keywords:} Reactant concentration, Nanophase ZnFe$_2$O$_4$, IR spectroscopy, Magnetic moment, SQUID magnetometer

\textbf{1 Introduction}

The study of nanoparticle systems has been a subject of continuous interest in physics as well as in other disciplines\textsuperscript{1-4}. Spinel ferrites are materials of great interest because of their large number of technological applications. They provide an opportunity to understand theoretically the interactions at nanoscale\textsuperscript{5-7}. Of all the spinel systems, ZnFe$_2$O$_4$ is found to be the most interesting to study the effect of grain size on structural, morphological and magnetic properties\textsuperscript{8}. By virtue of magnetic properties, ZnFe$_2$O$_4$ and its solid solutions with other ferrites are widely used in electronic industry\textsuperscript{9}.

The structure of spinel oxides AB$_2$O$_4$ consists of a close packed fcc arrangement of oxygen atoms with two non equivalent crystallographic sites A and B with tetrahedral and octahedral coordination. For ZnFe$_2$O$_4$, Zn$^{2+}$ and Fe$^{3+}$ distribution at A and B sites within the structure can be represented by the formula [Zn$_{2\delta}$Fe$_{1-\delta}$]$_4$ [Zn$_{1\delta}$Fe$_{1+\delta}$]$_{10}$O$_{16}$, where $\delta$ is the inversion parameter. In the case of normal spinel\textsuperscript{9,10} $\delta = 1$ and for inverse spinel $\delta = 0$. For partly inverted spinel $\delta$ is in between 0 and 1. The crystalline bulk form of ZnFe$_2$O$_4$ is a normal spinel with Zn$^{2+}$ ions only on the A sites and Fe$^{3+}$ ions only on the B sites and is characterised as an ordered antiferromagnet below 10K\textsuperscript{8}. Recent investigations of nanocrystalline ZnFe$_2$O$_4$ have suggested that the cation distribution in this material is partly inverted and exhibits anomaly in its magnetisation\textsuperscript{6,8}. Magnetic studies on nanophase ZnFe$_2$O$_4$ by many workers reported that they are ferrimagnetically ordered with high ordering temperature and high magnetic moment\textsuperscript{6,8,11-13}.

In the past few years several workers investigated stoichiometric zinc ferrite nano particles\textsuperscript{6,14,15}. It is a known fact that particle size and morphology of the powders may be controlled by the reaction conditions. Particle property such as particle size and morphology greatly affect its material property\textsuperscript{16}. The size reduction of a magnetic material leads to novel properties as compared to bulk material due to the small volume (superparamagnetism) or the high surface to volume ratio (spin canting)\textsuperscript{15}.

It has been found that ferrite particles of similar composition differ in their magnetic properties depending on the preparation technique. In this study, nanophase ZnFe$_2$O$_4$ has been prepared at low temperature under different reactant concentration conditions by co-precipitation. Investigations on structural and magnetic properties of ZnFe$_2$O$_4$ are carried out by IR spectroscopy and SQUID magnetometer measurements. IR spectroscopy is an important tool, which provides qualitative information regarding structural details of crystalline materials\textsuperscript{17-19}. The results from IR absorption study can be used to interpret the magnetic properties of ferrites\textsuperscript{20}. The absorption bands from which the details regarding the functional groups and their linkages can be explored are found to be dependent on atomic mass, cationic radius, cation-anion bond distances and cation
distribution. The effect of particle size on IR absorption and magnetic property of ZnFe$_2$O$_4$ by studying the cation distribution has been investigated. Magnetic measurements have been carried out using SQUID magnetometer in the range 5 to 300K and the magnetic moment variations with annealing temperature (particle size effect) have been investigated. Also it has been seen that whether these two analysis results are complimentary to each other.

2 Experimental Details

Zinc ferrite was prepared by co-precipitation method at room temperature as described by Sato et al. The materials used were aqueous solution of Zn(NO$_3$)$_2$, aqueous solution of Fe(NO$_3$)$_3$ and liquor ammonia(NH$_4$OH). ZnFe$_2$O$_4$ nanoparticles were prepared for different reactant concentrations (0.002 mol L$^{-1}$, 0.01 mol L$^{-1}$, 0.1 mol L$^{-1}$) under stoichiometric conditions. 0.1M ZnFe$_2$O$_4$ was prepared by adding 100 ml 0.1M aqueous solution of Zn(NO$_3$)$_2$ to 100 ml 0.2 M aqueous solution of Fe(NO$_3$)$_3$ in a conical flask under constant stirring using a magnetic stirrer. While stirring this mixture, 25% liquor ammonia was added until the pH was in between 9 and 11 at room temperature. The precipitate formed was washed several times with distilled water, filtered, dried in an oven at 90$°$C and annealed at 150$°$C for 2 h. Different samples of 0.1 mol L$^{-1}$ ZnFe$_2$O$_4$ were annealed at temperatures 300, 500, 700 and 850$°$C for 2 h to vary the particle size. The finely prepared powder is used for the study of TEM, XRD, IR, TG/DTA and SQUID magnetometer analysis. XRD profiles were taken by Philips (1710 PW) powder X-ray diffractometer using CuK$_\alpha$ radiation over a wide range of Bragg angle. The FTIR spectrum in the mid-IR and far-IR range was taken by Bruker IFS 66V FTIR spectrometer. Measurements of magnetization against temperature in field-cooled (FC) and zero-field cooled (ZFC) modes were performed in a SQUID magnetometer between 5 and 300K for 3 samples. TEM imaging of the powder sample of 0.1 mol L$^{-1}$ ZnFe$_2$O$_4$ annealed at 150$°$C was carried out in a Philips CM-200 analytical transmission electron microscope working at 120KV. Thermal analysis of the sample (0.01 mol L$^{-1}$) was carried out in a TG/DTA instrument, 92-18 (SETARAM) in Argon atmosphere at a heating rate of 10$°$C/min.

3 Results and Discussion

Fig. 1 shows the TEM image and the corresponding electron diffraction pattern of ZnFe$_2$O$_4$ powder of 0.1 mol L$^{-1}$ reactant concentration annealed at 150$°$C. It has been observed that the particles are not aggregated, having almost uniform size distribution and the average size is about 4 nm (Fig. 1). Electron diffraction pattern shows circular rings, which are characteristics of nanocrystalline materials. Fig. 2 shows the XRD pattern of 0.1 mol L$^{-1}$ sample annealed at different temperatures. The formation of single-phase cubic spinel ZnFe$_2$O$_4$ was confirmed by the XRD pattern (JCPDS No. 22-1012). It reveals that
the increase of annealing temperature yields the sharpness of the peaks, i.e., the increase of the grain size as well as crystallinity with annealing temperature\textsuperscript{21}. Table 1 gives the estimated grain diameters obtained using Scherrer method. The particle size (4 nm) of 0.1 mol L\textsuperscript{-1} sample at 150°C is found to be identical with the size determined by TEM imaging. Table 2 shows the variation of particle size with reactant concentration measured by XRD technique. It is found that the reactant concentration has only a minor role in varying the particle size compared with the effect of annealing temperature.

Figures 3 and 4 show the mid-IR and far-IR absorption spectra of 0.1 mol L\textsuperscript{-1} sample annealed at different temperatures (150-700°C). In the normal zinc ferrite, there are four ($\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$) infrared lattice vibrations. The high frequency bands ($\nu_1$ and $\nu_2$) are very sensitive to changes in interaction between oxygen and cations in octahedral and tetrahedral positions\textsuperscript{18,19} and frequently appear in the ranges 600-540 and 450-400 cm\textsuperscript{-1}. The low frequency band $\nu_3$ normally appears close to 330 cm\textsuperscript{-1}\textsuperscript{18,19}. The bands $\nu_3$ and $\nu_4$ correspond to divalent as well as oxygen and thermal vibrations respectively\textsuperscript{20}. From Fig. 3, it has been observed that as temperature increases the intensity of O-H vibration of water molecules (1640 cm\textsuperscript{-1}, 3400 cm\textsuperscript{-1}) decreases ie, complete elimination of water content takes place around 500°C and the crystallization of the spinel phase of ZnFe$_2$O$_4$ takes place\textsuperscript{18,19}, which is also evident from TGA/DTA curve. In our study $\nu_1$ band starts at 568 cm\textsuperscript{-1} and decrease to 541 cm\textsuperscript{-1} as the particle size increases. This is a consequence of size effect. For nanoparticles, small changes in the environment of a chemical group will lead to small changes in the characteristic vibrational frequencies for this group. Here as the particle size decreases the increase in frequency (blue shift) is observed\textsuperscript{3,22,23}. Similar behaviour is observed for frequencies $\nu_2$, $\nu_3$ and $\nu_4$. The frequency $\nu_2$ varies from 404 to 369 cm\textsuperscript{-1}, $\nu_3$ varies from 325 to 322 cm\textsuperscript{-1} and $\nu_4$ varies from 168 to 164 cm\textsuperscript{-1} (Fig. 4). In far-IR spectrum no vibrations are observed when the particle size is 4nm, being annealed at 150°C having low crystallinity. At low temperatures the intensity of vibrations are not enough to be detected due to the amorphous nature evident from XRD. The intensity of the peaks increases with annealing temperature due to the increase in crystallinity as is clear from XRD. The change in position of $\nu_3$ is very small.

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<th>Table 1—Variation of particle size with annealing temperature</th>
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<td>Annealing temperature (°C)</td>
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<th>Table 2—Variation of particle size with reactant concentration</th>
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<td>Reactant concentration</td>
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<td>0.002 mol L\textsuperscript{-1}</td>
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<td>0.01 mol L\textsuperscript{-1}</td>
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<td>0.1 mol L\textsuperscript{-1}</td>
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Fig. 3—Mid-IR spectrum of 0.1 mol L\textsuperscript{-1} ZnFe$_2$O$_4$ annealed at different temperatures

Fig. 4—Far-IR spectrum of 0.1 mol L\textsuperscript{-1} ZnFe$_2$O$_4$ annealed at different temperatures
compared to other wave numbers. The same behaviour was observed for ZnFe$_2$O$_4$ in the earlier report\textsuperscript{18}. The variation in the band position may be due to variation in the cation-oxygen bond length\textsuperscript{17}. It was reported that $\nu_3$ band is assigned to divalent [Zn$^{2+}$] octahedral metal ion-oxygen group complexes\textsuperscript{17}. This is an indication that in nano phase ZnFe$_2$O$_4$, there is partial inversion of lattice sites and octahedral lattice sites are partly occupied by Zn$^{2+}$ ions. Also the broadening of $\nu_2$ band with decrease in particle size may be due to the occupancy of cations of the different characters on the same site\textsuperscript{17,24}. From these observations it can be assumed that as the particle size decreases, the inversion nature of the spinel ferrite increases.

Figure 5 shows the mid-IR spectra of 0.002 mol L$^{-1}$, 0.01 mol L$^{-1}$ and 0.1 mol L$^{-1}$ samples annealed each at 300°C. A wave number change has been observed from 559 to 549 cm$^{-1}$ as the reactant concentration increases.

This may be attributed to the change in particle size and hence the metal ion-oxygen bond distances\textsuperscript{17}. Figure 6 shows the TGA and DTA curve of ZnFe$_2$O$_4$ (0.1 mol L$^{-1}$) nanoparticles. From TGA curve a weight loss of 20% was observed over the temperature region 50-250°C. From 250°C onwards there is a small weight loss $\approx$ 1.5% upto 600°C. The endothermic peak at the onset temperature of 386°C in the DTA curve corresponds to the crystallisation of the spinel phase of ZnFe$_2$O$_4$ nanoparticles\textsuperscript{18,19}. At the onset temperature of 685°C, a prominent exothermic peak is observed without any mass loss. This peak may be attributed to the recrystallisation and grain growth of ZnFe$_2$O$_4$ nanoparticles\textsuperscript{18}. The particle size changed from 6 nm to 28 nm when the temperature increased from 300 to 850°C as is clear from XRD pattern. The microstructure and atomic configuration of nanoparticles change when exposed to high temperature since the free energy of these particles is higher than that of bulk crystalline counterpart.

The magnetization (emu/gm) values were measured with temperature under FC and ZFC conditions for three samples (6, 12 and 21 nm) and plotted as in Figs 7-9. It is found that the ZFC magnetization increases with decrease in temperature reach a broad maximum and then decreases. The temperature dependence of the magnetization for nanocrystals can be expressed as $M_s(T)=M_s(0)(1-\beta T^b)$ where $M_s$ is the saturation magnetization, $\beta$ the Bloch constant and $b$ the Bloch exponent\textsuperscript{25}. Theoretical calculations showed that a finite particle size can cause an appreciable deviation from $T^{3/2}$ law for ferro or ferrimagnets at low temperature\textsuperscript{26}. The magnetization peak in ZFC curve occurs corresponding to the blocking temperature of superparamagnetic particles\textsuperscript{14,15,27}. Below this temperature the magnetic susceptibility decreases with decrease in $T$. Such behaviour is characteristic of superparamagnetism exhibited by nanoparticles. The peak value is 24 emu/gm for 6 nm particle, 22 emu/gm for 12 nm particle and 2.6 emu/gm for 21 nm particle. But the nature of FC curve is found to vary with particle size. In the case of 6nm particle (Fig. 7), after reaching maximum value of magnetization, the FC curve remains horizontal being unaffected by decrease in temperature. Saturation magnetization can be attained for particles with average diameter $\sim$ 6nm and such behaviour are attributed to surface effects\textsuperscript{27}. Temperature dependant FC branch occurs as a result of sizable interaction or aggregation in nanoparticles.
But in the case of 12 nm particle (Fig. 8), there is a small broad peak in FC curve. For 21 nm particle (Fig. 9), the FC peak becomes narrow and identical with ZFC curve with slight separation between them below the peak temperature (blocking temperature).

More often, interparticle dipolar and/or exchange interaction plays an important role in determining a magnetic collective behaviour\textsuperscript{28,29}. In the case of non-stoichiometric zinc ferrite, the FC peak was attributed to a decrease in magnetic interactions due to the inclusion of zinc ions in ferrite matrix\textsuperscript{30}. It has been found that in the case of cobalt ferrite, for 4.7 nm particles, the FC branch is rather flat and this has been assigned to the result of sizable interaction or aggregation effects\textsuperscript{27}. Thus it has been revealed that large interactions induce a plateau not far below the separation between FC and ZFC curves without any peak. Also it is made clear that the separation between FC and ZFC curve is a measure of the interactions among Fe ions\textsuperscript{27,30,31}. This is true in the case of 6 nm particles. As particle size decreases the occupancy of tetrahedral A site by Fe\textsuperscript{3+} increases, thereby increasing the interactions between Fe\textsuperscript{3+} ions on A and B sublattices causing high value of magnetic moment. With increase in annealing temperature, the particle size increases, decreasing the occupancy of Fe\textsuperscript{3+} ions on A site and thus reducing exchange interactions. This is clearly seen in FC curve of Fig. 8, which shows a broad peak and Fig. 9 a narrow peak with FC and ZFC nearly coinciding. Thus the inversion nature of nano zinc ferrite is supported by IR spectroscopic study and magnetization measurements.

For a particular system, the superparamagnetic transition temperature (blocking temperature) $T_B$ depends on the particle size and anisotropy energies\textsuperscript{10}. In this study the blocking temperature $T_B$ is found to be approximately 35°C for 6 nm, 50°C for 12 nm and 30°C for 21 nm particles (Figs 7-9). Blocking temperature increases from 35 to 50°C when the particle size increases from 6 to 12 nm. But in the case of 21 nm particles obtained by annealing the sample at 700°C, there is an anomaly showing a decrease in $T_B$ against the expectation of increase in blocking temperature. But it was reported that in the case of zinc ferrite thin films, when the film was annealed at 650°C, a decrease in blocking temperature was observed\textsuperscript{32}. It was explained as due to oxygen deficiencies, which cause rearrangement of zinc and oxygen atoms leading to the magnetic change. From the DTA curve (Fig. 6) the exothermic peak at 685°C shows the recrystallisation and grain growth process of ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles. Therefore it is made clear that due to recrystallisation, a magnetic change is produced in the sample, which causes a decrease in $T_B$ and decrease in magnetic moment.

\section*{4 Conclusions}

The reactant concentration of ZnFe\textsubscript{2}O\textsubscript{4} sample prepared by co-precipitation has little effect on particle
size. Though the particle size variation with reactant concentration is small, a considerable change in IR absorption spectroscopic wave number is observed. IR spectroscopy is used to explain the inversion mechanism of nanophase ZnFe$_2$O$_4$ spinel and its magnetic properties. Magnetization measurement using SQUID magnetometer has revealed that small particles of ZnFe$_2$O$_4$ are highly interacting due to super exchange interaction between Fe$^{3+}$ ions on two sublattices A and B and support IR spectroscopic study. Thus the inversion nature of nano particle ZnFe$_2$O$_4$ was proved by IR spectroscopic and magnetic studies.

References