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Influence of a particular temperature on zinc ferrite

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ABSTRACT

Zinc ferrite has been prepared by co-precipitation route to maintain pH-12 of the precipitation solution at a particular temperature 600°C. The physical and chemical properties of the nanomaterials depends on their size and shape or morphology. Particle size of the co-precipitated material is strongly dependent on the method of preparation and experimental conditions. The synthesized samples were characterized using XRD, FTIR, TEM and by VSM in ZFC and FC environment.

Keywords: Zinc ferrite; co-precipitation; XRD; FTIR; TEM; VSM.

1.Introduction

Nanosized magnetic particles, which possess drastically different properties from that of their corresponding bulk materials have renewed interest in the last decade with increasing possibilities of applications in the field of nanostructured materials technology. The study of nanoparticle system has been a subject of continuous interest in physics as well as in other disciplines. The synthesis of nanomgnetic materials has been a field of extensive research, due to novel propertie. 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. Ferrites are magnetic materials, which exhibit high electrical resistivity, low eddy currents, and low dielectric loss and are extensively used in microwave devices, computer memories and magnetic recordings. Spinel ferrites are materials with good magnetic and electronic properties, which depend strongly on the cation distribution among the tetrahedral and octahedral sites. Quantum size effects and the large surface area of magnetic nanoparticles dramatically change some of the magnetic properties and exhibit superparamagnetic phenomena and quantum tunnelling of magnetization, because each particle can be considered as single magnetic domain. Among the spinel ferrite systems, zinc ferrite (ZnFe₂O₄) is found to be most interesting to study its structural, morphological and magnetic properties [1]. The structure of spinel oxides AB₂O₄ consists of a closed packed FCC arrangement of oxygen atoms with two non-equivalent crystallographic sites A and B with tetrahedral and octahedral coordination. In case of $ZnFe_2O_4$, Zn^{2+} and Fe^{3+} distribution at A and B sites within the structure can be represented by the formula

$$\left[\operatorname{Zn}_{\delta}\operatorname{Fe}_{1-\delta}\right]^{A}\left[\operatorname{Zn}_{1-\delta}\operatorname{Fe}_{1+\delta}\right]^{B}O^{4},$$

where δ is the inversion parameter. For normal spinel system $\delta = 1$ and for inverse spinel system $\delta = 0$ [2,3]. For partly inverted spinel system lies in between 0 and 1. The crystalline bulk form of ZnFe₂O₄ is a normal spinel with Zn^{2+} ions only on the A sites and Fe^{3+} ions only on the B sites and is characterized as an ordered anti-ferromagnet below 10 K [1]. Superparamagnetism is a unique feature of magnetic nanoparticles and has great relevance to modern technologies including magnetic resonance imaging



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contrast agents, data life time in high density information storage, ferrofluid technology and magnetic refrigeration. In this work we analyzed the magnetic properties of zinc ferrite powders synthesized by the co-precipitation[4,5] technique. In this technique, particle size, chemical homogeneity and degree of agglomeration can be easily controlled.

2 Experimental

2.1 Preparation of samples

The zinc ferrite samples have been prepared by co-precipitation technique followed by heat treatment at different temperatures. The high purity reagents (Aldrich 99.99% purity): zinc nitrate $Zn(NO_3)_2.6H_2O$, ferric nitrate $Fe(NO_3)_3.2H_2O$, sodium hydroxide NaOH and distilled water were used to prepare the samples. ZnFe2O4 nanoparticles were prepared by adding 0.1 mol of zinc nitrate in 500 ml distilled water and 0.2 mol of ferric nitrate in 500 ml distilled water in a conical flask under constant stirring using a magnetic stirrer. During stirring the sodium hydroxide was added drop wise to maintain the pH of solution at about 10 at reaction temperature of 343K. The precipitate so formed was washed several times with distilled water and then filtered. The powder was dried in an oven at 373K. The prepared powdered sample of zinc ferrite was annealed at different temperatures 873K for 4h.

2.2 Characterization of samples

Complementary methods were used to characterize the heat treated $ZnFe_2O_4$ samples. In order to determine the crystallite size and lattice constant, XRD patterns of samples were recorded by an X-ray diffractometer (Philips PW/1710) with Cu filter using monochromatic CuKa radiation of wavelength 1.548 Å at 50 KV and 40 mA, in the scanning range $2\theta \sim 10-80^{\circ}$. To investigate the particle size distribution and morphology of the samples, TEM micrograph was recorded using transmission electron microscope (Hitachi-H7500) at 100 KV. For this purpose, samples were dispersed in ethyl alcohol in an ultrasonic bath and then pipetted on a carbon-coated copper grid. To study the compositional characteristics from optical excitation of vibrational modes, infrared spectra were recorded in the range 4000-400 cm⁻¹ using Fourier transform infrared spectrometer (Perkin Elmer 1600). For this purpose, pellets were obtained by homogeneously mixing the samples with KBr powder and then pressing. The saturation magnetization measurements were carried out by a search coil method. Polytronic power supply (model-BCS-1000), electromagnet (Type Hem-100) and flux meter (model-FM109) were used for this purpose.

3 Results and discussions

3.1 XRD studies:

Fig.1 illustrates the XRD patterns of as prepared sample thermally treated at different temperatures 873K for 4 h. The diffraction pattern of as prepared sample shows broad peaks centered around 20^{\sim} 30.08, 35.42, 42.96, 53.26, 56.78, 62.32° and their respective Miller indices could be compared with standard XRD pattern of zinc ferrite. Chekcell program has been used to determine Miller indices (220), (311), (400), (422), (511), (440) of observed peaks in XRD patterns. The broad peaks suggest the good crystallinity of prepared sample. The XRD pattern of sample exhibits sharp peaks. It has space group Fd3m (cubic-0.8441nm, space group: Fd3m, Z=8; [ICDD PDF:22-1012] [6-8]. Here, it is worth mentioning that the traces of naturally occurred phases like Fe₂O₃ and ZnO in the pattern of zinc ferrite samples are absent. The absence of additional impurity phase formation, which is generally observed in ferrites synthesized by the conventional ceramic method [6-9], indicates that the co-precipitation results in the better quality samples having no impurity phases.



Fig.1

The crystallite size has been determined by the well known Debye-Scherrer formula [10]:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is a constant (=0.9), D is the crystallite size in nm, β is the full width of the diffraction line at half of the maximum measured in radian, θ is the X-ray wavelength in nm and θ is the Bragg angle corresponding to a peak. The observed crystallite size is 30 nm and the observed lattice parameter is 8.4208Å of the sample annealed at 873K.

The X-ray density of a ferrite sample D_{f} has been determined by the following relation [11]:

$$D_f = \frac{8M}{N a^3}$$

Where M is the sum of atomic weights of all the atoms in the unit cell (i.e. the molecular weight of zinc ferrite), N is the Avogadro's number and a³ is the volume of cubic unit cell. Each unit cell of the spinel structure contains eight molecules. The X-ray density of prepared sample is 595.45gm/cm³.

3.2 FTIR studies

The infrared spectra of annealed sample has been investigated to obtain the information of structure and the arrangement of building structural groups with respect to each other and the types of bonds present in the sample. The assignment of infrared absorption bands are influenced by the oxidation state of the sample.



Fig. 2

As shown from figure, two important absorption bands below 600 cm⁻¹ is present. The IR bands are assigned as v_1 and θ_2 respectively. The figure show that the band θ^1 representing the A-site lies around 550 cm⁻¹ and band θ_2 corresponding to Bsite lies around 430 cm⁻¹ [12]. The FTIR spectra of sample was recorded in the wavenumber range of 400-4000 cm⁻¹. In this spectrum, 550 and 430 cm⁻¹ are typical characteristic bands of zinc ferrite [13], in which higher frequency bands attributes to intrinsic vibration of Zn-O (tetrahedral site) while lower frequency bands correspond to stretching vibration of Fe-O (octahedral site) [14,15]. This spectrum also shows H-O-H band overtones with the surface hydroxyl group vibration and results in the broadening of band around 1600 cm⁻¹. The band around 1300 cm⁻¹ is due to the banding modes of H-O-H absorbed at the surface. A very strong and broad band centred at 3387 cm⁻¹ can be assigned to the peaks of H₂O. As the absorption band has an inverse relationship with the bond length, it is expected that the absorption band θ_2 will be less as compared to θ_1 band as experimentally observed. The absorption bands observed within these specific frequency limits reveal the formation of mixed spinel structure.

3.3 TEM studies

TEM was employed to visualize the size and the shape of crystallites and to confirm the nano crystalline nature of the prepared samples. Fig. 6 shows the TEM images of zinc ferrite samples calcined at temperature 873K K. The micrographs of prepared samples reveal the compact arrangement of almost homogeneous nanoparticles with spherical shape. The images clearly show the agglomeration of nanoparticles which may be attributed to the magnetic dipole interactions between the particles. The particle size determined from TEM is 34nm which is in agreement with the particle size determined from XRD. This suggested that several neighbouring particles fused together to increase the particle size due to the melting of their surfaces [16].



Fig. 3

3.4 Magnetization studies

The magnetic properties of the prepared $ZnFe_2O_4$ nanoparticles calcined at 873K was investigated by the VSM technique in the range of -5000 to +5000 Gauss and magnetization values were measured with temperature under ZFC and FC as shown in figure 4,5,6 respectively. The samples exhibited modified ferromagnetic magnetic behavior. The room temperature magnetic behaviour of ferrite nanoparticles, which were fabricated by co-precipitation technique, can be explained as the results of important factors such as cationic distribution in spinel structure, the heating rate of calcination, and the surface spin structure of nanoparticles.



The values of retentivity (M_r) , coercivity (Hc) and saturation magnetization (M_s) of the sample are 0.30, 210.2 ,0.7 emu/g respectively. Cation inversion is one of the most important parameters that can be effective in the variation of the magnetic properties of zinc ferrite nanoparticles from that of their bulk counterparts. In bulk form, zinc ferrite has a normal spinel structure in which all the Zn^{2+} ions are in A-sites and Fe^{3+} ions are distributed in B-sites [17]. Morever, in bulk form, zinc ferrite only occurs in intrasublattice (B-B) exchange interactions and it does not have intra-sublattice (A-A) exchange interactions or inter-sublattice (A-B) super exchange interactions [18]. The inter-sublattice (A-B) super exchange interactions of the cations are much stronger than the (A-A) and the (B-B) interactions at nanoscale [19]. Due to cation inversion, which originates from heat treatment, the structure of ZnFe₂O₄ transfers from a normal spinel structure to a mixed spinel structure [18]. This cation inversion causes the zinc ferrite nanoparticles to experience intra-sublattice (A-B) super exchange interactions and intra-sublattice (A-A) exchange interactions in addition to intra-sublattice (B-B) exchange interactions .It is found that the ZFC and FC magnetization decreases with decreases in temperature. But after 0°C ZFC and FC curve remains horizontal being unaffected by decrease in temperature .The ZFC and FC curve is a measure of the interactions among Fe ionsThus the inversion nature of zinc ferrite is supported by magnetic measurements.







4. Conclusions

The present study explores the synthesis of pure nanocrystalline spinel zinc ferrite by co-precipitation method. The structural and magnetic properties of zinc ferrites depend on experimental conditions. XRD patterns and TEM images show the formation of ZnFe2O4 nanoparticles having particle size in aggrement with each other. FTIR confirmed the presence of zinc ferrite phase in the sample. The magnetic properties of ZnFe2O4 nanoparticles suggested that co-precipitation method is a useful technique to design and fabricate novel magnetic materials. Further, this method can be extended to the synthesis of other spinel ferrite nanoparticles of technological importance.

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