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Influence of Co^{2+} distribution and spin–orbit coupling on the resultant magnetic properties of spinel cobalt ferrite nanocrystals

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ABSTRACT

Superparamagnetic properties of the cobalt ferrite nanocrystals have been demonstrated. The significance of the solgel autocombustion method in preparation of cobalt ferrite oxide in the nano range (30–40 nm) has been very well complimented with the structural, dimensional and morphological techniques, such as X-ray diffraction technique, Transmission Electron Microscopy and Scanning Electron Microscopy. The valence states of the metal ions and single phase formation of the polycrystalline oxide have been confirmed with the help of X-ray photoelectron spectroscopy and Raman spectroscopy. The distribution of the Fe^{3+} ions in the tetrahedral and octahedral lattice sites has been illustrated with the help of the Mössbauer spectroscopy that shows five sextets, indicating occupancies of one tetrahedral and four octahedral sites by Fe^{3+} ions. Hyperfine fields of 51.29, 48.74, 46.78, 43.58 and 48.59 Tesla, respectively in $CoFe_2O_4$ have been found for four octahedral and one tetrahedral site respectively, at ambient temperature. The magnetic measurements *M*–*H* and *M*–*T* demonstrate a change in the magnetic moment and a superparamagnetic–ferrimagnetic transition at 235 K in the ferrite system.

1. Introduction

Magnetic spinel ferrites are of great technological interest and have grabbed the attention of many researchers due to their fascinating electromagnetic properties. The ease of preparation and the stability of these materials under various conditions have added lot of significance for their use in the industry. The novelty observed in the physico-chemical and the electromagnetic properties due to changes in the particle dimension and composition has encouraged researchers around the globe to synthesize these materials [1–7]. The exotic magnetic, electronic and magneto-optical properties of the cobalt ferrite ($CoFe_2O_4$) have prioritized them in the manufacturing of magnetic recording devices, magnetic refrigeration, catalysis, sensors and magnetic fluids [8,9]. Magnetic nanocrystals have been of great interest over the past several years for the fundamental understanding of nanomagnetism and for their technological and biomedical applications [8–12]. Single phase magnetic ferrites and their nanocomposites find tremendous application as antimicrobial agents and vehicle for drug delivery, thus proving their vitality even in the non-technological field, thereby expanding their horizon of application [13–15]. The magnetic properties of nanocrystals vary greatly with changing dimensions and superparamagnetism is a typical example of such a size-dependent behavior at the nanometer scale. Different applications such as technical and medical, demands different set of magnetic properties. Therefore, approaches aiming at the synthesis of ferrite oxides with uniform particle size are essential for controlling the magnetic properties to satisfy the requirements for such applications. Systematic studies on the correlations between magnetic properties and the chemical compositions of nanocrystals will generate invaluable insight towards the fundamental understanding of magnetic properties and consequently enable to identify suitable candidates of magnetic nanocrystals for various applications. Over the years, the magnetic nanoparticles that have been studied are mostly the iron containing oxides, particularly magnetite (Fe_3O_4) which could be due to its easy availability. Now, with the advancement in nanoscience and nanotechnological research, new types of magnetic nanocrystals have become available.

$CoFe_2O_4$ belongs to the crystal family of spinel ferrites (AB_2O_4). The magnetic properties of these oxides are mainly dominated by the distribution and the magnetic interaction of the cations in the two lattices, i.e., tetrahedral (A) and the octahedral (B). Because of the difference in the strengths of magnetic interactions at these two lattices of the spinel oxides, the magnetic properties possessed by $CoFe_2O_4$ nanocrystals vary with change in the cation distribution, thereby generating scope for the various applications. $CoFe_2O_4$ crystallizes as random spinel which can be represented as $(Co_x^{2+}Fe_{1-x}^{+3})[Co_{1-x}^{2+}Fe_{1+x}^{3+}]O_4$, where *x* depends on the thermal history and the preparation conditions. A systematic study of the

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significance of the method used in the preparation of $CoFe_2O_4$ nanocrystals would provide insights towards better understanding of the correlations between the particle dimension, spin orbit (*L*–*S*) coupling and the magnetic properties. Consequently, the desirable magnetic properties for technological/biomedical applications can be optimized through chemical changes which are sensitive to the preparation issues such as method, reaction conditions, particle size distribution and the occupancy of the two lattices by the metal ions.

Sol–gel autocombustion method is among the best method and used due to its effectiveness in obtaining the desired monophasic products with greater homogeneity and finer particle size at very low sintering temperatures [16–18]. However to achieve the compositional homogeneity of the final oxide powder, the preparation of a homogenous gel with respect to the distribution of cations is crucial. Therefore, it is essential to prepare a suitable precursor solution which can be converted to a gel without any cation segregation. The usage of malic acid and ethylene glycol as complexing and gelling agents at a neutral pH for the sol–gel assisted combustion synthesis of $CoFe_2O_4$ is reported herein. The effect of pH on the chelating action of the organic acid is demonstrated, which is vital in preventing the precipitation and aggregation of the ions and maintaining the homogeneity of the solution [19]. A detailed investigation about the influence of distribution of the metal ions (Co^{2+} and Fe^{3+}) in the crystal lattice and the dimensions of the ferrite oxide on the resultant magnetic properties is reported in this article. The contribution of *L*–*S* coupling, from Co^{2+} ions, towards higher magnetic anisotropy and hence the magnetic properties is investigated. The results provide an insight on the inter-relationship of the particle dimension, the *L*–*S* coupling and the resulting superparamagnetic property. The conclusions on structural and magnetic properties have been aptly supported by the magnetic and spectral data obtained from various characterization techniques and the results prove $CoFe_2O_4$ nanoparticles to be a suitable candidate in the technological and biomedical applications.

2. Experimental

2.1. Preparation

For the synthesis of $CoFe_2O_4$, stoichiometric amounts of analytical grade $Co(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich) and $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma–Aldrich) were utilized and were brought into solution by dissolving in double distilled water. The solution was maintained around 100 °C with continuous stirring. Calculated amount of malic acid was than added. pH of the solution was then increased (around neutral) with the slow addition of 30% ammonia solution. A considerable change in color from light pink to dark wine red was observed which confirmed the chelating action of malic acid. The dependence of chelating action on pH, seems to be very high as there was no chelation and hence gel formation observed at lower pH values. It can be said that the higher pH (around neutral), forces the organic acid to release the acidic proton and in turn bind with the available metal ions. After confirming the pH, ethylene glycol in the ratio 1:4 (with respect to the malic acid) was added. The solution was then allowed to concentrate with continuous stirring and the gel so obtained was heated in an oven at a temperature of about 200 °C for 3 h. Formation of a voluminous foamy precursor was observed which was then crushed into fine powder with the help of an agate mortar and pestle. The precursor was than calcined at 400 °C for 4 h. It was again ground with acetone and after drying was sintered at 600 °C for 6 h. The as-obtained powder was than subjected to various characterization techniques.

2.2. Characterization

The crystallinity, crystal structure and the phase purity of the powders were investigated by X-ray diffraction (XRD) technique using Cu Kα radiations of wavelength 1.5418 Å (filtered through Ni), in steps of 0.02° on a RIGAKU ULTIMA IV X-ray diffractometer. SHIMADZU FTIR PRESTIGE-21 spectrophotometer was put into use to record the FTIR spectrum of the oxide calcined at 600 °C. A comparative study of the Raman and IR actives modes was done. Raman spectrum was recorded in the backscattering geometry in the range 100–1000 cm^{-1} using a HORIBA JOBIN YVON HR-800 Raman spectrometer with an Olympus microscope (objective 50*x*) attachment and equipped with a CCD detector. A 488 nm Ar^+ ion laser with 10 mW powers was used as the excitation source for a spot of about 1 mm in diameter. Morphology analysis of the compound was carried out on JEOL JSM-6360 LV Scanning Electron Microscope (SEM). Transmission Electron Microscopy (TEM) images were recorded on PHILIPS CM 200 Transmission Electron Microscope operating at an accelerating voltage of 200 kV and providing a resolution of 2.4 Å. Particle size distribution study of the as prepared nanoparticles was carried out by employing a DELSA NANO S, BECKMAN COULTER, USA. The valence state and binding energies of various chemical species were determined by the X-ray photoelectron spectroscopy (XPS) employing VSW SCIENTIFIC INSTRUMENT with Al Kα as the incident source having energy of 1486.6 eV with a resolution of 0.9 eV. The vaccum maintained in the sample analyzer chamber was 1.4×10^{-8} Torr. ^{57}Fe Mössbauer measurements were performed in transmission mode with a ^{57}Co radioactive source in constant acceleration (triangular wave) mode using a standard PC based Mössbauer spectrometer (Nucleonix Systems Pvt. Ltd., Hyderabad, India). Velocity calibration of the spectrometer was done with an enriched α-^{57}Fe metal foil absorber at room temperature and the isomer shift values were given relative to Fe foil. The outer line width of calibration spectrum was 0.29 mm s^{-1}. The recorded Mössbauer spectrum was fitted by using the WinNormos fit programme. A QUANTUM DESIGN PPMS-VSM magnetometer was used for magnetic characterization of the pelletized compounds. The variation of the DC-susceptibility of each sample with temperature was measured from 5 K to 300 K in the ZFC (zero field cooling) and FC (field cooling) modes using a magnetic field of 10 KOe. The magnetization with varying magnetic field of up to 50 KOe was also measured at 5 K and 300 K.

3. Results and discussion

3.1. Structural analysis

Fig. 1a shows the X-ray diffractogram of $CoFe_2O_4$ sintered at 600 °C for 6 h. All the diffraction peaks observed for the oxide corresponds to the cubic spinel ferrite structure. The phase analysis was carried out by matching the obtained diffractogram with the standard ICDD card number 22-1086. The XRD pattern reveals the monophasic formation of the polycrystalline compound and also signifies its greater crystallinity. A higher peak width which is obvious from the XRD peaks signifies that the compound comprises of finer particles. The broadening of the peaks also indicates the decrease in the density and an increase in the surface to volume ratio of the $CoFe_2O_4$ nano oxide. The unit cell parameter (*a*) is calculated for the $CoFe_2O_4$ system as a Voigt function for the (3 1 1) peak. Crystallite size and the lattice strain present in the system are calculated from the X-ray diffractograms. Williamson–Hall extrapolations as a Lorentzian function are very well utilized in calculating these parameters. Williamson–Hall plot for $CoFe_2O_4$ is shown in Fig. 1b. A microdistortion of 2.7×10^{-2} is present in the $CoFe_2O_4$ structure. This may be accompanied with the migration of Co^{2+} ions from the tetrahedral to the octahedral lattice. This process of migration decreases the induced lattice strain, thereby stabilizing the crystal structure [16]. The average crystallite size and the lattice constant (*a*) obtained for the $CoFe_2O_4$ system from the X-ray diffraction is 8 nm and 8.390 Å. The value for the lattice constant is in agreement with the reported value [8].

3.2. Morphology and chemical analysis

The SEM micrograph of $CoFe_2O_4$ sintered at 600 °C is presented in Fig. 2. The image displays a flaky and porous morphology for the oxide ferrite. The micrograph confirms the formation of secondary particles or lumps of aggregates which may be due to the agglomeration of the primary particles. Consistency in the ferrite phase formation is seen for the sample which is equally supported by the results obtained from XRD.

3.3. Particle size analysis

The TEM images of $CoFe_2O_4$ along with the electron diffraction pattern are presented in Fig. 3a–c. The images reveal the partially fused nature of the hexagonal particles with an average particle size of 40 nm. The variation in particle size is prominently seen for the oxide. The well crystallized nature of $CoFe_2O_4$ along with