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Low Curie-transition temperature and superparamagnetic nature of Fe_3O_4 nanoparticles prepared by colloidal nanocrystal synthesis

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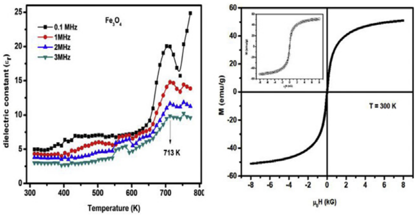
HIGHLIGHTS

- Fe_3O_4 nanoparticles are synthesized by "colloidal nano-crystal synthesis" technique.
- The particles size found to be (12 nm) from transmission electron micrographs.
- Low dielectric loss of 0.015 is suitable for low noise device application.
- The lowest Curie transition temperature (T_c) of 713 K is reported.
- At room temperature Fe_3O_4 nanoparticles shows superparamagnetic nature.

GRAPHICAL ABSTRACT



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ABSTRACT

Colloidal size, narrow size-distributed magnetite (Fe_3O_4) nanospheres of 12 nm diameter were synthesized by colloidal nanocrystal synthesis protocols. X-ray diffraction and transmission electron microscopy studies reveal that the as-synthesized magnetite particles were single grain, spherical shaped and well crysallined in cubic spinel structure. Lattice vibrational studies confirms the existence of metal-oxide nanospheres and organic functional group (oleic acid) present on the particles surface. The nanospheres exhibits slightly enhanced energy band gap compared to counterpart bulk. The sample shows space-charge type polarization under low electric field frequencies (0.1–3 MHz) in the high temperature range (305–790 K), with Curie temperature at 713 K. Hence the dielectric constant (ε') reduces with enhance of electric field frequency. Dielectric loss (ε'') also reduces with enhance of frequency and the loss is 0.015 upto 650 K under 3 MHz. Hence it may be suitable for low loss device applications. AC electrical conductivity (σ_{ac}) enhances with frequency and polaron hopping is slower than the site relaxation. Temperature dependent impedance spectra analysis reveals that grain contribution is predominant than grain boundary contribution with Debye-type relaxation. The nanospheres exhibits typical superparamagnetic behaviour with reduced saturation magnetization (M_s) due to disordered spins on the nanospheres' surface. Langevin function fit gives 10.5 nm magnetic domain diameter in the nanospheres.

1. Introduction

Iron oxides are well known as magnetic materials and its nanoparticles are used in various applications, e.g., magnetic data

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storage devices, catalysis, sensors, biomedical [1]. However, for these applications a well crystallined and monodisperse nanoparticles are required for high efficiency. Therefore researchers were developed various bottom-up nanoparticles synthesis protocols such as coprecipitation [2], polyol [3], hydrothermal [4], solvothermal [5], colloidal nanocrystal [6], etc., for ferrites (iron oxides) nanoparticles. In addition, top-bottom approach such as mechanical milling (ball milling) of bulk samples into nanoparticles. The prepared nanoparticles show modified magnetic properties such as superparamagnetism, enhanced or reduced saturation magnetization (M_s) compared to their counterpart bulk. In superparamagnetic nanoparticle the magnetic moment of all the spins orient in a single direction but its magnetic energy (μ.B) is less than thermal energy (k_BT) at room temperature. Hence the net magnetization of a group of superparamagnetic nanoparticles becomes zero due to random thermal fluctuations [7].

Among all iron oxides, magnetite (Fe_3O_4) shows high M_s due to: (i) antiferromagnetic exchange across tetrahedral (Fe^{3+}) sublattice and octahedral (Fe^{2+} & Fe^{3+}) sublattice; (ii) no cation vacancies in the lattice, whereas maghemite (γ-Fe_3O_4) has cation vacancies. Magnetite crystallizes in inverse spinnel structure. In the past one decade, Fe_3O_4 nanoparticles with different morphologies, chemical substitutions and surface coatings were applied to many applications such as magnetic resonance imaging (MRI) contrast agents [8,9], drug delivery [10], tissue repair [11], *in-vivo* applications such as detoxification of biological fluids, immunoassay, cell variation and hyperthermia [12] and microwave applications at high and low frequencies [13]. It is also used as cores in inductors and transformers [14]. Further, new phenomenon such as magnetodielectric coupling were observed [15]. Magnetite nanosphere are synthesized by various protocols as mentioned earlier. Among all the methods reported, colloidal nanocrystal synthesis protocols produce very narrow size distribution and well crystallined nanoparticles [6,16]. It successfully produced colloidal size semiconductor nanocrystals (quantum dots) as well as binary and ternary oxides. It is known that colloidal size nanocrystals show superparamagnetic nature with reduced magnetic Curie temperature (T_C) due to small crystallite size. To the best of our knowledge there is no detailed report on dielectric, ac-conductivity and magnetic studies on small size magnetite nanospheres synthesized by colloidal nanocrystal synthesis protocols. We report the above mentioned studies on magnetite nanospheres to find their suitability in microwave device applications. The Magnetite nanospheres were synthesized with relatively narrow size distribution and high crystallinity by colloidal nanocrystal synthesis protocols. Magnetic susceptibility (χ), ac-conductivity and electric permittivity (ε) properties of the nanospheres were studied by varying the experimental parameters. We found that the magnetite nanospheres shows low Curie temperature and less dielectric loss upto 650 K.

2. Experimental details

2.1. Materials used

The starting materials were Fe(III)acetylacetonate or $Fe(acac)_3$ (solid, 97%, Sigma-Aldrich), oleylamine (liquid, 65%, SDFCL), oleic acid (liquid, 70%, Aldrich), benzyl ether (liquid, 98%, Aldrich, boiling point 298 °C), absolute ethanol (liquid, 99%, Sigma-Aldrich) and n-hexane (liquid, 95%, Sigma-Aldrich). All the chemicals were used as received.

2.2. Synthesis of Fe_3O_4 nanoparticles

In order to synthesize magnetite nanocrystals, 50 mL of benzyl ether (BE) solvent were taken in a three neck round bottom (RB) flask with condensorat centre neckand septa at side ports. Oleic acid (OA) and oleylamine (OAm) of 5 mL each were added to the BE solvent and stirred for 10 min with magnetic stirrer to get homogeneous solution. Then 2.2880 g of $Fe(acac)_3$ powder was added to the reaction mixture. The resultant solution were heated to 120° C with hemispherical heating mantle, kept on magnetic stirrer, to produce heat by Joule heating by altering its input voltage. Kept at this temperature for 30 min to remove water from the reaction flask. Then the condensor was filled with circulating water and raised the reaction mixture temperature to reflux point of BE (298 °C) at 5 °C per min. heating rate. The solution was refluxed for 1 h and then naturally cooled the black coloured solution with iron oxide particle to room temperature. The black nanoparticles were precipitated by addding anti-solvents such as ethanol, acetone, etc., here ethanol is used as precipitator. The precipitate was separated from the solution by sedimentation through centrifugation. The iron oxide particles were washed and dispersed in good solvents such as toulene, n-hexane, chloroform. Here n-hexane was used. The precipitation and dispersion process were repeated two more time to remove excess surfactants from the oxide particles.

2.3. Characterization of Fe_3O_4 particles

The structure and phase purity of the Fe_3O_4 were studied by powder X-ray diffraction technique using Diffractometer (Bruker, D8 Advance) with Cu Kα radiation (λ = 1.54056 Å). The FT-IR spectrum of the sample was recorded in the energy range of 4000–4,00 cm^{-1} by FT-IR spectrophotometer (IR Affinity-1, Shimadzu). The optical excitation spectrum of the sample was recorded by UV–Vis–NIR spectrophotometer (V-670 PC JASCO) in the diffuse reflectance mode and energy bandgap is estimated from it. The morphology and crystallinity of the sample were studied by transmission electron microscope (JEM–2100, JEOL). The electric permittivity measurements the sample were studied by commercial LCR meter (LCR HiTESTER 3532-50, HIOKI). The electrodes were mounted on two opposite face of regular geometry of the sample with suitable thickness of silver paste to make good conduction. The magnetic properties of the sample were studied through magnetic hysteresis loops and were measured by Vibrating Sample Magnetometer (Lakeshore VSM-7410).

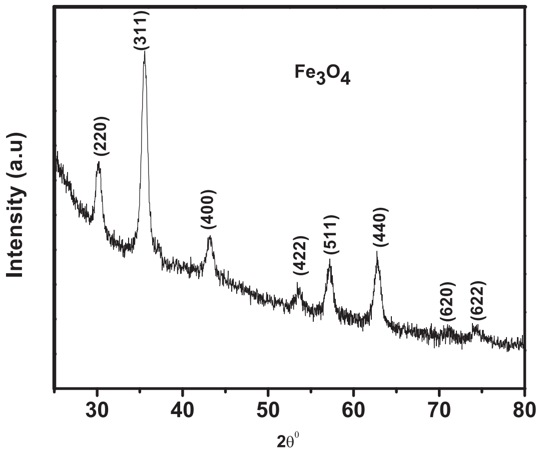

Fig. 1. The X-ray diffraction profile Fe_3O_4 powder.