Materials Chemistry and Physics 164 (2015) 183–187

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

A study of dielectric, optical and magnetic characteristics of maghemite nanocrystallites

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HIGHLIGHTS

- Synthesis of maghemite nanoparticles using coprecipitation pyrolysis method.
- Spherical shaped 25 nm particle size achieved with homogeneous and uniform size distribution.
- Study of low and high frequency dielectric response of maghemite nanoparticles.
- A UV/Vis optical band gap of 2.3 eV was obtained which is larger than the bulk sample value.
- Room temperature (300 K) and 77 K magnetic studies of nanomaghemites.

ARTICLE INFO

Article history:
Received 21 April 2015
Received in revised form
24 June 2015
Accepted 15 August 2015
Available online 29 August 2015

Keywords:
X-ray diffraction (XRD)
Dielectric properties
Optical band gap
M–H loop

ABSTRACT

The maghemite (γ-Fe_2O_3) nanocrystallites have been synthesized by a co-precipitation pyrolsis method through 3 h annealing at 275 °C. Structural characterization measurement (X-ray diffraction) confirmed nanoparticles to be in pure maghemite phase with a particle size (as estimated through Scherrer formula) to be 27 nm. Scanning electron microscope (SEM) image confirmed the average particle size to be almost 25 nm with an almost spherical morphology and uniform distribution. In the dielectric measurements (which is the key novelty of this work), we observe a steep decrease in the dielectric constant at the low frequencies which can be attributed as a Maxwell–Wagner type effect. Whereas, at higher frequencies dielectric constant becomes almost frequency independent which can be regarded as a relaxation time phenomena. In the optical characteristics, the band gap of nano-maghemites has been calculated from the absorption spectra in the ultraviolet–visible (UV–Vis) range, which turns out to be 2.3 eV. Finally, in the magnetic measurements we performed a magnetization versus applied field (M–H) loop at the room temperature as well as 77 K. We notice an increasing trend in the values of saturation magnetization (Ms) and coercive field (Hc) as a function of applied temperatures. At room temperature (77 K) Ms and Hc values are found to be 50.4 (56.5) emu/g and 202.4 (248.6) Oe respectively, which manifests a suppression of thermal randomization of magnetic moments of maghemite nanoparticles with decreasing temperatures.

1. Introduction

Nanoscience has emerged as a revolution both in science and in technology since the last decade of the twentieth century [1]. Starting from the 1952 R. P. Feynman's seminal talk [2], the field has proved to be interdisciplinary, where ideas from physics, biology, chemistry, material science and engineering are merging together to better understand, control and manipulate the properties of matter at the nanoscale. The scientific literature is full of disparate experimental methods for the manufacturing and understanding the behavior of the nanomaterials, which exists in different dimensions, shapes and geometries [3]. In this context, chemically synthesized nanoparticles have their own distinct importance due to their versatile applications based on their electrical, optical and magnetic properties [4,5], which shows novel and astonishing behaviors in contrast to their bulk counterparts [6]. In the last decade,

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http://dx.doi.org/10.1016/j.matchemphys.2015.08.041
0254-0584/

the synthesis of iron oxide magnetic nanoparticles (MNPs) has greatly increased because of their broad range of applications from: magnetic storage media industry [7], biosensing [8], medical agents in targeted drug delivery [9,10], contrast agents in magnetic resonance imaging (MRI) [11,12] and magnetic inks for jet printing [13]. MNPs are also widely used for catalytic purpose [14] where photo catalysts utilize photon energy to carry out oxidation and reaction reductions [14,15].

Among various iron oxide phases, maghemite (γ-Fe_2O_3) nanoparticles have been extensively studied due to their non toxicity, biocompatibility, thermal and chemical stability and favorable magnetic properties [17]. It is known that nanoparticles possess large chemically active surface area and presence of variety of bonds in maghemite make them suitable for the coating of bioactive molecule. Drugs, protein, enzymes and antibodies can be attached to MNPs and then these particles can be targeted to an organ, tissue and tumor by the application of strong magnetic fields [9]. Usually the surfactant reduces the magnetic moment of the bare nanoparticles and cannot be used efficiently in magnetic data storage devices and biomedical applications where strong magnetic response is required. Therefore, uncoated MNPs have still great potential for commercial applications. Consequently, either coated or uncoated MNPs must have large saturation magnetization, moderate coercivity, high blocking temperatures and uniform size and shape distribution [16].

A number of approaches have been employed for the synthesis of small sized (5–15 nm) maghemite nanoparticles with controlled surface shape morphology. Some compelling examples include the preparation of maghemite nanoparticles through: microemulsion method [17], direct thermal decomposition of Fe–urea complex [18] and magnetite nanoparticles [19], aerosol pyrolysis [20], ball milling technique [21], sol gel method [22] and LASER pyrolysis method [23]. For example, in two recent experiments Q. He et al. has demonstrated one pot synthesis technique to prepare iron oxide nano chains [24] and achieved morphology and phase controlled stabilization with Maleic Anhydride Grafted polypropylene [25].

Among these synthesis approaches, co-precipitation (or the wet-chemical) route has several advantages such as homogeneity, low cost, less time consuming, ultra-pure precursors without annealing and enhanced controllability of particle size and morphology by optimizing chemical reaction parameters and annealing time, rate and atmosphere [26–28]. For instance, in our recent work [29], we chemically synthesized superparamagnetic maghemite nanoparticles (of 15 nm size) using the coprecipitation approach with annealing the sample for 3 h at 200 °C. In that work, we focused on the effect of temperature variation on the dielectric response of the superparamagnetic nanomaghemites, whereas in present work we study the optical, dielectric and magnetic properties of the nanomaghemites with considerably larger average size (25 nm).

Keeping in view the aforementioned advantages and the requirements for applications, in this work we have synthesized maghemite nanoparticles by co-precipitation method and studied their physical properties. It is worthwhile to emphasize here that the magnetic and optical properties of maghemite nanoparticles have already been reported in the past when particles are prepared using different preparation routes [9,30,31]. The main novelty of our work is the dielectric measurements of our nanomaghemites samples which to our knowledge have not been reported in the present context.

2. Experimental

In the present paper maghemite nanoparticles are synthesized through co-precipitation pyrolysis method following the procedure: As the first step of precipitation, appropriate amounts of Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) in 2 M HCl and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were mixed at room temperature ($Fe^{2+}/Fe^{3+} = 1/2$) and 200 ml of 1.5 M NaOH solution was added, under vigorous stirring for about 30 min, using a magnetic stirrer till pH level of 11 was obtained. Next the precipitates were washed five times with deionized water to remove impurities. To separate the precipitate from impurities the mixture was centrifuged for one minute at 2000 rpm (revolutions per minute). After repeating the last step twice, the sample was dried at 40 °C [32]. The acquired substance was finally grinded into a fine powder and then annealed at 250–500 °C for three hours in steps of 25 °C. The annealing was performed in the air atmosphere with an annealing rate of 5 °C/minute.

3. Results and discussion

3.1. XRD analysis

The structure and phase purity of the sample were confirmed by performing powder x-ray diffraction (XRD) with Cu K_α radiation of $\lambda = 1.5405$ Å at room temperature. We used the XRD model JDX-11 of Joel Company Ltd. Japan, operated at 35 KV and 20 mA. The crystallite size was calculated using Scherer's formula.

Maghemite phase is known to be very sensitive to the annealing times and temperatures. After many trials, we came to the conclusion that for the present preparation technique, an impurity free maghemite phase can be obtained through 3 h annealing at 275 °C. X-ray diffraction pattern of maghemite sample is shown in Fig. 1a. As can be seen that all peaks and their intensity (specifically the ones indicated by the miller indices at (311), (222) and (440)), are the standard maghemite peaks. Particle size was calculated from all major peaks using the following Scherer formula:

$$t = \frac{K\lambda}{\beta\cos\theta} \tag{3.1}$$

where K (Shape Factor) = 0.91, λ (Wavelength of X-Rays) = 1.5406 Å; β, θ and t are the line broadening at half the maximum intensity (FWHM) in radians, Bragg's angle, and the mean size of particles respectively. Crystallite size is calculated from each peak and then an average size is obtained which in the present case turned out to be size 27 ± 1 nm.

3.2. SEM analysis

To further confirm the particle size and to observe the shape and morphology of our sample we have performed the SEM analysis and the result is shown in Fig. 1 (b). We notice that the uniformly distributed and homogeneous spherical maghemite nanoparticles have been achieved using this synthesis technique. The particle size lies in the range of 25 nm which agrees with the particle size estimated from the Scherrer formula (XRD analysis). Hence SEM shows the present method of synthesis (under mentioned annealing conditions) achieves its main aim of producing nanomaghemites with controlled shape and size. Note that in the bottom full scale line equals 500 nm such that the separation between two tick marks on the scale is 50 nm.

3.3. Dielectric properties

The dielectric properties of γ-Fe_2O_3 were measured by experimental setup (four probe LCR meter) with frequency up to 1 MHz that consists of a capacitance bridge with three terminal networks and a crystal holder. The specimen, in the form of a pallet of 1 mm