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Particle size effect on Mössbauer parameters in γ-Fe_2O_3 nanoparticles

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ABSTRACT

Nanoparticles of maghemite (γ-Fe_2O_3) were synthesized by chemical co-precipitation method for different particle size ranges and Mössbauer spectroscopy was employed to see the particle size effect on the Mössbauer parameters, especially on the average internal magnetic field of the system. It was observed that the internal magnetic field increased with increase in particle size. The contribution of superparamagnetic component for all size ranges is almost equal, i.e. 10%, while the relaxed subspectrum contributes around 50% at all stages. The superparamagnetic component was a quadrupole doublet up to 40 nm and then it transformed into a singlet at larger particle sizes. This indicates that the electric field gradient vanishes for this particular Fe environment and has an ideal cubic symmetry.

1. Introduction

Development in the synthesis of nanoparticle materials stems from their fundamental and technological importance, as they exhibit electrical, optical, and magnetic properties that are different from their bulk counterparts. Surface effects become more and more important as the particle size decreases, because the surface to volume ratio increases. The surface magnetic properties result basically from the breaking symmetry of the lattice, which leads to site-specific, generally unidirectional surface anisotropy, broken exchange bonds, which in turn results spin disorder and frustration, especially in ferrimagnets [1]. The increased surface area to volume ratio in small particles is of great importance in surface-sensitive catalysts. Particle size dependence of the physical properties of magnetic materials is also a well-known phenomenon. In recording media like magnetic tapes a suitable choice of coercivity and resonance is the basis for the use of small particles, as well as for the increased information density. The particle size effects enable tailoring the materials to a wide range of applications. Interest is increasing day by day due to the observation that materials with nano-sized particles exhibit novel electronic, magnetic, optical, chemical, and bio-medical properties [2–5]. The unique combination of high magnetization and paramagnetic nature of these materials makes them to have a wide range of applications. Particularly, the possibilities of nanoparticle modification by biologically active compounds to be used in controlled drug delivery systems, as agents in the magnetic resonance imaging and for magnetic-induced tumor treatment via hyperthermia are very interesting [6]. Iron oxide-based nanoparticles belong to the most widely used materials in this field, although they have worse magnetic properties, lower saturation magnetization, and lower specific loss of power than Fe and Co nanoparticles, which have recently started gaining attention for bio-medical purposes, too [7]. Iron oxides nanoparticles have many advantages over these materials, e.g., better oxidative stability, compatibility in non-aqueous systems, and non-toxicity. Among the four crystalline polymorphs of iron (III) oxide, α-Fe_2O_3 as hematite, β-Fe_2O_3, γ-Fe_2O_3 as maghemite, and ε-Fe_2O_3, maghemite has gained the greatest interest in the above mentioned applications [4,8]. Maghemite is also a technologically important compound widely used for the production of magnetic materials and catalysts [9]. It is an iron oxide mineral, with composition similar to ferric oxide (Fe_2O_3), and exhibits strong magnetism and remanence. Its structure is isometric, of defective spinel form, and somewhat iron-deficient. Maghemite is metastable with respect to hematite and forms a continuous metastable solid solution with magnetite, as for example titanium can substitute for iron, giving rise to titanomaghemite. Natural maghemite is formed by the oxidation of magnetite.

A variety of methods are being used for the preparation of synthetic maghemite, e.g. the ceramic method, the co-precipitation method, the sol–gel method, crystallization with a melting method, etc. [10]. The motivation of the present work was to synthesize iron oxide nanoparticles of various sizes, which have very important technological applications in the field of bio-medical, recording media, electronics, etc. We also want to check the effect of size variation on the magnetic behaviour of these nano-sized materials. In the present study samples are prepared

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by the chemical co-precipitation method. Mössbauer spectroscopy is a very effective and sensitive technique to find the particle size effect and the spin structure to study the super-transferred hyperfine interactions in nanostructured materials. A Mössbauer spectrum can be characterized by hyperfine parameters like internal magnetic field (H_{eff}), quadrupole splitting (Δ), and isomer shift (δ). The effect of interactions between iron containing nanoparticles on superparamagnetic relaxation can also be studied very effectively by Mössbauer spectroscopy because these interactions can sense minute changes in the local crystalline structure and in the magnetic properties of the system [11–15].

2. Experimental

Maghemite nanoparticles were prepared by the co-precipitation method. Initially 200 mL of purified, deoxygenated water was bubbled by nitrogen gas for 30 min. Then 5.3 g $FeCl_3$ and 2.0 g $FeCl_2$ were dissolved in the above mixture and was stirred mechanically. In the protection of nitrogen gas, 1.5 M NH_4OH solution was added drop-wise into the above mixture under vigorous stirring. Initially brown precipitates and thereafter black precipitates were formed. When the pH value reached 8.0, the stirrer was turned off and the magnetite settled gradually. The black precipitates were isolated by an external magnetic field of 3000 G with the supernatant decanted. To obtain the pure and neutral products, synthesized materials were rinsed with ultra-pure water three times. Finally, magnetite nanogel was obtained by adding 1 mL of 25% tetramethylammonium hydroxide into the precipitates. To obtain the maghemite nanogel, freeze-dried magnetite particles were dispersed in 99% octyl ether and the mixture was then heated to 250 °C under an air atmosphere and maintained at this temperature for 2 h. Red–brown γ-Fe_2O_3 nanogel was collected via external magnetic field after adding ethanol. Mössbauer data collection was carried out at room temperature using a ^{57}Co (Rh-matrix) source of initially 25 mCi strength, in transmission geometry. Mössbauer spectrometer was calibrated using a thin α-Fe foil. Data analysis was performed using a computer program Mos-90 [16], assuming that all the peaks are Lorentzian in shape. X-ray diffraction studies were carried out on an X-ray diffractometer with CuKα radiation (1.5406 Å) with 2θ ranges from 25° to 70°, step size of 0.02°, and scanning speed of 1 °/min. The dimensions of synthesized materials were examined by transmission electron microscopy (TEM) (JEOL-2010). Diluted maghemite was coated on copper grid covered with a thin carbon layer. The copper grid was then dried for 24 h in a desicator before carrying out the TEM studies.

3. Results and discussion

In order to confirm the crystal size, XRD and TEM were performed and the pertinent/corresponding results of one of the samples are shown in Figs. 1 and 2. In X-ray powder diffraction, the peaks matched well with standard γ-Fe_2O_3 reflections (JCPDS card # 39-1346). The increase in peak width confirms the presence of nano-sized particles. Applying Scherer's equation on 311 peak, we obtain $d = K\lambda/\beta \cos\theta$ where K is the shape factor and is selected 0.94 for cubic samples, λ is the X-ray wavelength, β is the FWHM in radians, and θ is the Bragg angle. The average particle size d is around 13 nm, which is in close agreement with the TEM results shown in Fig. 2.

Mössbauer spectra of maghemite for different particle size ranges are shown in Fig. 3. These spectra are of complex nature and consisted of magnetic sextets, relaxed magnetic components and superparamagnetic subspectra including a quadrupole doublet or a singlet. In the bulk material domain walls are created minimizing the magnetic stray energy. Whereas in case of small particles, having diameter in nanoscale each grain may be a magnetic domain. Therefore, the anisotropy energy will be proportional to the volume of the grain, which may show the paramagnetic nature, even if the material is ordered magnetically, so called superparamagnetism. In this case the spectrum will be obtained just like a paramagnetic material. Fig. 3(a) shows the Mössbauer spectrum of γ-Fe_2O_3 for the 10–20 nm range. It is

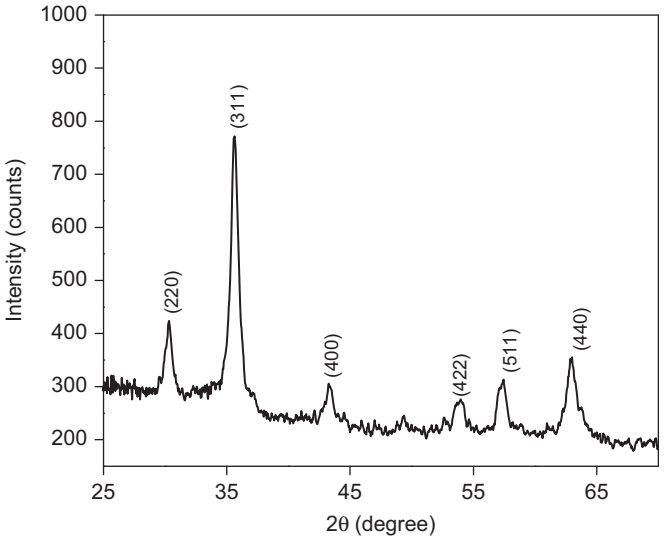

Fig. 1. X-ray diffraction pattern for 10–20 nm particle size range.

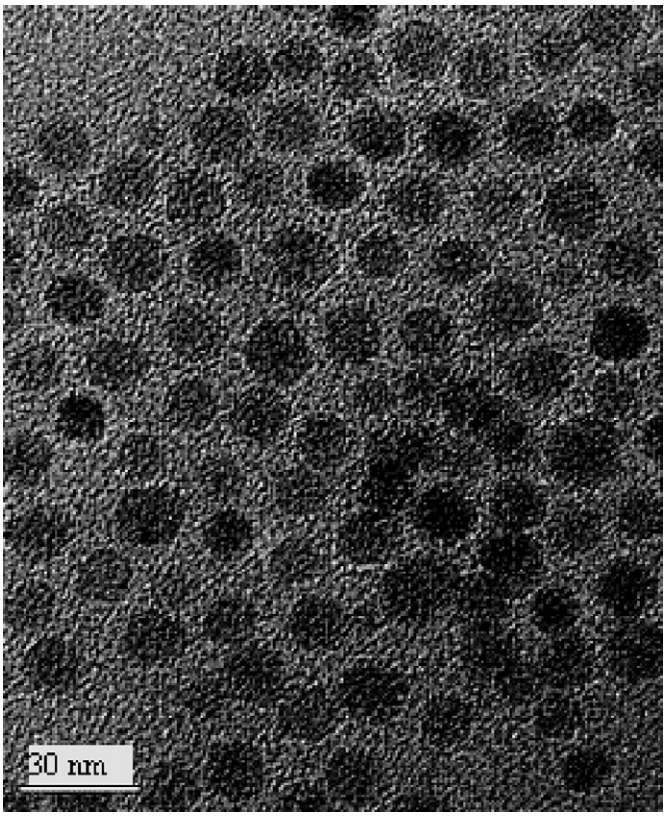

Fig. 2. TEM image of 10–20 nm particle size range.