Journal of Non-Crystalline Solids 400 (2014) 45–50

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effect of amorphous silica matrix on structural, magnetic, and dielectric properties of cobalt ferrite/silica nanocomposites

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ARTICLE INFO

Article history:
Received 26 February 2014
Received in revised form 7 April 2014
Available online 21 May 2014

Keywords:
Nanoparticles;
Glass–ceramic composites;
Ferrites

ABSTRACT

Effect of amorphous silica (SiO_2) matrix concentration on structural, magnetic, and dielectric properties of $(CoFe_2O_4)_{1-y}/(SiO_2)_y$ nanocomposites with y (SiO_2 concentration) = 10, 30, 50 and 60% was studied in detail. $CoFe_2O_4$ nanoparticles dispersed in SiO_2 matrix were prepared by using sol-gel method. X-ray diffraction (XRD) analysis revealed the spinel ferrite structure for all the samples. The average crystallite size was decreased with SiO_2 concentration (y) due to large number of nucleation sites formed by SiO_2 matrix during synthesis (for the formation of nanoparticles), which finally restricts the particle growth. Fourier transform infrared (FTIR) spectroscopy confirmed the formation of spinel ferrite and SiO_2 matrix. Scanning electron microscopy (SEM) images showed that the particles are spherical in shape and less agglomerated. The magnetization was decreased on increasing the SiO_2 concentration and is attributed to diminishing of the particle size with SiO_2 concentration. Smaller nanoparticles exhibit lower magnetization as compared to larger nanoparticles due to disordered surface spins. Dielectric constant, loss tangent and imaginary part of dielectric constant all showed decreasing trend with increasing frequency due to inability of the space charge carriers to keep with the alternation electric field, while ac conductivity increases with increasing frequency. All dielectric parameters also showed dependency on SiO_2 concentration and were decreased with increasing SiO_2 concentration. The reduction of magnetic and dielectric properties is attributed to diminishing of crystallite size with increasing SiO_2 matrix concentration. Therefore SiO_2 matrix can be useful in controlling the nanoparticle size and dielectric as well as magnetic properties of the ferrite nanoparticles.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) nanoparticles have got the attention of scientist due to their vast applicability especially in microwave region. They are magnetic, dielectric and exhibits low eddy current losses. Cobalt ferrite has large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and a mechanical hardness, which are desirable for many practical applications [1,2]. As the technology is miniaturizing to nanoscale, materials with flexible properties are needed for applications such as cobalt ferrites [3–5].

Cobalt ferrite has cubic spinel structure with 8 divalent, 16 trivalent metal cations and 32 oxygen anions in a unit cell [1,6]. The unit cell of $CoFe_2O_4$ is the repetition of tetrahedral and octahedral cubic structures. There can be two types of iron cations in ferrites such as Fe^{2+} and Fe^{3+}. Divalent iron ions prefer tetrahedral while trivalent ions prefer octahedral sites. Magnetic spins at tetrahedral and octahedral lattice sites are antiparallel to each other. There are different efforts made to improve the dielectric as well as magnetic properties of the cobalt ferrite through various doping [7–9]. Dielectric properties determine the behavior of electromagnetic waves in the medium [10]. Shinde et al. [11] studied dielectric properties of Si doped $CoFe_2O_4$ as a function of temperature and reported an increase in dielectric constant with temperature. Gopalan et al. [12] studied dielectric properties of $CoFe_2O_4$ nanoparticles prepared by using sol-gel method and exhibited lower values of dielectric constant as compared to bulk cobalt ferrite. Gul et al. [13] studied the effect of Al substitution on dielectric properties of nanocrystalline $CoFe_2O_4$ and found decreased dielectric constant for higher Al concentration. Rana et al. [14] studied the Gd substituted $CoFe_2O_4$ nanoparticles and found increased dielectric properties with Gd concentration. Kumar et al. [15] reported a decrease in dielectric loss with Mn concentration and decreasing particle size at higher reaction time for Mn substituted $CoFe_2O_4$ nanoparticles. Above literature describes the doping effects in cobalt ferrite but there is not much about the detailed study of the dielectric and magnetic properties of cobalt ferrite nanoparticles/matrix nanocomposites.

At nanoscale, cobalt ferrite properties depend upon synthesis techniques, chemical composition, annealing or sintering time, particle size, temperature, and doped material [16,17]. Also the interparticle interactions between the magnetic nanoparticles can modify their individual magnetic behavior. Bare magnetic nanoparticles usually agglomerated due to strong magnetic interparticle interactions. To

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.05.004
0022-3093/

reduce these magnetic interactions, different matrices can be used to avoid interparticle interactions [18,19]. Non-magnetic silica is an important compound used for coating purpose to prevent nanoparticles agglomeration, improve chemical stability of the nanoparticles and biologically friendly for targeted drug delivery. Also the non-magnetic silica does not influence the magnetic properties of the cobalt ferrite nanoparticles as well as their dielectric properties due to its smaller dielectric constant. The $CoFe_2O_4/SiO_2$ nanocomposites with controlled magnetic and dielectric properties could be beneficial for biological and high frequency applications. In this article, we studied the effect of SiO_2 matrix concentration on structural, magnetic, and dielectric properties of cobalt ferrite nanoparticles.

2. Experiment

Cobalt ferrite/silica nanocomposites were prepared using standard sol-gel technique. Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were mixed in ethanol in respective stoichiometry (solution 1). Another solution 2 was prepared containing citric acid and distilled water in a molar ratio of 1:4. Then solution 2 was mixed drop wise in solution 1 under stirring and heating at 80 °C. After mixing both solutions, tetraethyl orthosilicate (TEOS) was added drop-wise which acts as a precursor for SiO_2 matrix. We added different amounts of TEOS (a precursor of SiO_2) equal to 10, 30, 50 and 60% of the weight of total nitrates (iron nitrate and cobalt nitrate) to prepare nanoparticle samples with different concentration of silica matrix. Now ammonia was added to adjust the pH value to 5. The combined solution was kept at 80 °C until the formation of gel. The gel is dried overnight at 100 °C to remove water and ethanol contents. The dried gel was then crushed into fine powder and annealed at 900 °C for 2 h to form the required single-phase $CoFe_2O_4$ nanoparticles dispersed in SiO_2 matrix [20]. Structural characterization includes X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Magnetic measurements were done by using vibrating sample magnetometer (VSM). Dielectric measurements were done at room temperature by using LCR meter. In the following, we define a parameter "y" which is the amount of TEOS (nominal SiO_2 concentration) equals to 10, 30, 50 and 60 wt.% of total nitrates. The samples are defined as $(CoFe_2O_4)_{1-y}/(SiO_2)_y$ nanocomposites with y (SiO_2 concentration) = 10, 30, 50 and 60%.

3. Results and discussion

Fig. 1(a) shows XRD pattern of $(CoFe_2O_4)_{1-y}/(SiO_2)_y$ (where $y = 10$, 30, 50, and 60%) nanocomposites with cobalt ferrite nanoparticles dispersed in silica matrix. For all the samples index peaks correspond to cubic spinel structure and there are no traces of impurities. There are no signatures of SiO_2 matrix in XRD due to its amorphous nature but a little hump between $2\theta^o = 20$ and 25 is present for higher concentrated silica samples. The most intense peak is (311) which is the preferred orientation of the planes in ferrites. The peak (440) sensitive to octahedral site is more intense than peak at (220) sensitive to tetrahedral. All peaks get broaden with increasing SiO_2 concentration (y) due to decrease in average crystallite size.

Average crystallite size was calculated by using Debye–Scherrer's formula using (311) peak and it lies in the range 25 nm–34 nm for different SiO_2 concentration (y). The Debye–Scherrer's formula is,

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the average crystallite size, λ is the wavelength of the X-ray radiation, K is a machine constant taken as 0.91, θ is the diffraction angle and β is the line width at half maximum height. Fig. 1(b) shows the variation of average crystallite size with SiO_2 concentration (y). It is evident that the average crystallite size is decreased with increasing SiO_2 concentration (y) due to large number of nucleation sites provided by

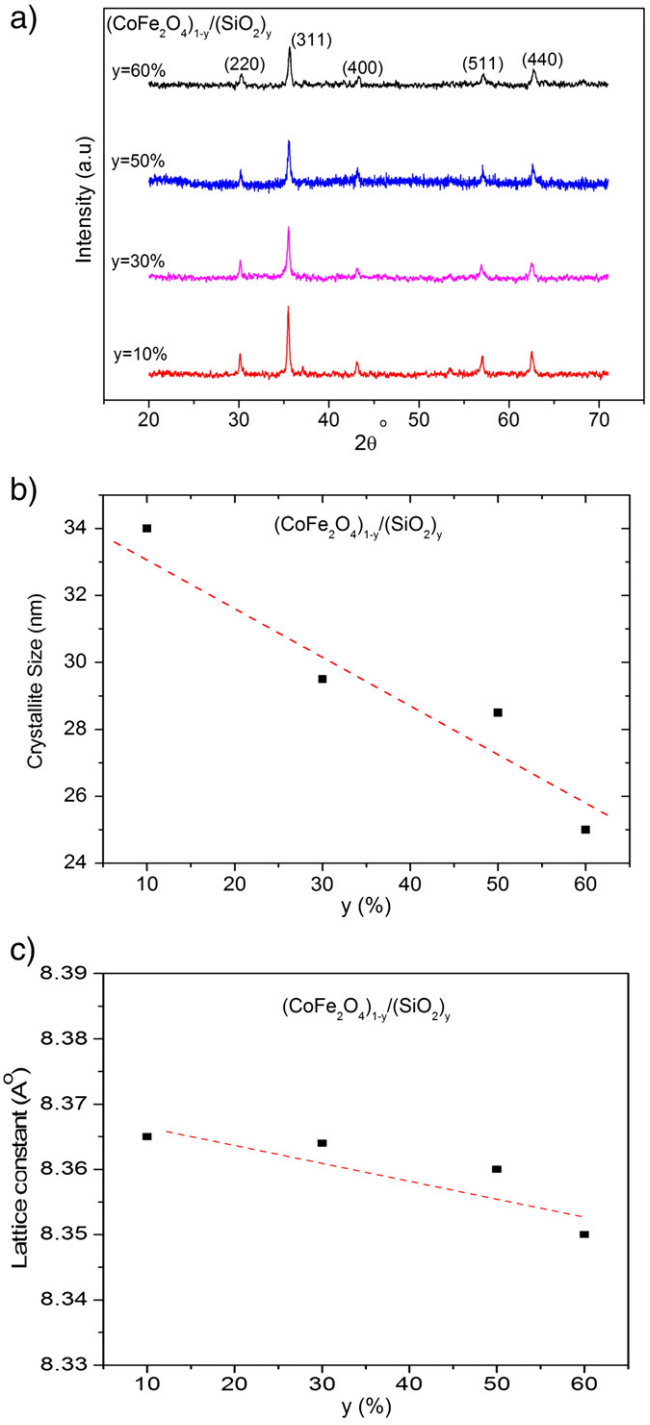

Fig. 1. X-ray diffraction patterns of $(CoFe_2O_4)_{1-y}/(SiO_2)_y$ nanocomposite samples with $y = 10, 30, 50$ and 60%, (b) average crystallite size as a function of SiO_2 concentration (y), and (c) lattice constant a as a function of SiO_2 concentration (y). Dashed line just shows the trend.

silica matrix (in higher SiO_2 concentrated samples), which restricts the particle growth [9].

Lattice parameter a was calculated by using formula:

$$a = d/\sqrt{\left(h^2 + k^2 + l^2\right)}. \quad (2)$$

Fig. 1(c) shows the variation of lattice parameter a as a function of SiO_2 concentration (y). A small variation in lattice constant a is observed with increasing SiO_2 concentration (y). The decrease in lattice constant